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PAH and PCB distribution in sediment fractions and sorptive phases

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PAH AND PCB DISTRIBUTION IN SEDIMENT FRACTIONS AND SORPTIVE PHASES

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For my father, who wanted to build bridges…..

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ABSTRACT

Contaminant distribution is integral to environmental evaluations of contaminated sediment on every level. The technical and economic feasibility of treatment or beneficial use is a function of the accessibility or separability of the contaminants within the sediment. The magnitude of release to the environment during dredging and disposal is dependent upon the partitioning behavior of the contaminants. Yet, little attention has been paid to contaminant distribution in the fine sediment fractions. Further, conventional distribution coefficients provide little information regarding the relative contaminant loading of each of the sorptive phases. Bioavailability of contaminants in oil and grease, soot and organic carbon, components of sediment total organic carbon (TOC), may be vastly different. Physical properties are also different and determine fate during treatment.

This study focused on the relative distribution of PAHs and PCBs in size and density fractions of three sediments, which were physically separated for direct measurement of contaminants in the fractions and correlation to sorptive phase distribution. Oil and grease, soot, (non-black carbon) organic carbon and mineral clay were measured in sediment fractions. Correlations between contaminant mass and the sorptive phases were established for a linear model using statistical analysis. From this model phase specific contaminant concentrations were obtained and contaminant reduction potential evaluated.

Contaminant concentrations were typically highest in oil and grease, soot, organic carbon, and clay, in that order. Black carbon and organic phases appear to be most important to PAH sorption. Clay appears to play a greater role in sorption of PCBs, although it was not significant for all sediments, and the influence of fine-grained organics on clay fraction sorption could not be distinguished without statistical analysis.

Phase specific distribution coefficients were calculated based on predicted contaminant concentrations in the sorptive phases. Typically oil and grease and soot coefficients were larger than organic carbon coefficients. The magnitude of the soot coefficients was generally higher for PAHs than for PCBs. Predicted coefficients showed little dependence on log K_{ow}, suggesting that in the natural environment, sorption of PAHs and PCBs is governed more by sorbent availability and steric effects, than by contaminant hydrophobicity.

CHAPTER 1

INTRODUCTION, BACKGROUND AND METHOD DEVELOPMENT

INTRODUCTION

When a navigation-dredging project is in the planning stages, all available alternatives are considered, including the no-action alternative and beneficial use alternative. Preliminary evaluation may involve primarily logistical concerns, from which the most viable alternatives emerge. These alternatives are then evaluated more intensively to identify the most cost efficient alternative that is environmentally protective. Fate and effects evaluations are major elements of these assessments. Decisions regarding the environmental acceptability of an alternative are based in large part upon the potential for exceedance of established environmental criteria. When definitive assessments are not possible, or criteria have not been established, biological testing and risk assessment may form the basis upon which a determination is made. In both cases, potential mobility and availability of contaminants is central to the analysis and is dependent upon reliable estimates of contaminant properties and behavior.

Distribution coefficients describe the partitioning of contaminants between solid and aqueous phases and are key elements in fate and effects evaluations. However, they are also subject to considerable uncertainty. Distribution coefficients may be derived based on bulk sediment properties and octanol-water coefficients, thermodynamic properties of the contaminant and sorptive phases, or sediment and pore water chemistry. Coefficient values reported for contaminants commonly found in navigation sediments may vary by as much as an order of magnitude or more, however, depending on the method of calculation. The outcome of an environmental analysis may therefore hinge on the value selected for the distribution coefficient. In the absence of better information, the most conservative values are typically utilized, resulting in environmental assessments that are protective, but possibly overly conservative.

Development of more global distribution coefficients has been the subject of much interest in the scientific community. Recent attention has been focused on the importance of soot, or black carbon, in sorption of hydrophobic organic contaminants. Other researchers have proposed that clay minerals may also play a role for these compounds. Based on previous studies, it appears that there are probably four phases of primary importance to contaminant distribution: oil and grease, soot, organic carbon and clay. While oil and grease is acknowledged to be an important phase for contaminant partitioning, little information has been published regarding the relative magnitude of partitioning to this phase in the presence of the others. Most published studies, in fact, have focused on one or two of these phases selectively, rather than the collective group.

Polynuclear aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) are anthropogenic contaminants commonly found in navigation sediments. This study utilized fractionation studies on natural sediments to measure contaminant concentrations in operationally defined sediment fractions. This data was used to evaluate the relative partitioning of these contaminants to each of the identified sorptive phases in the presence of the others, and to develop phase specific distribution coefficients. The data was also used to assess potential for contaminant reduction by separation of a specified size or density sediment fraction.

OBJECTIVES

The major objectives of this research effort were to 1) ascertain the distribution of PAHs and PCBs in three natural sediments with respect to operationally defined size and density fractions, 2) utilize the fractionation data to evaluate the correlation between contaminant distribution and distinct sorptive phases, 3) develop a model for phase specific distribution coefficients from the correlations, and 4) assess the utility of fractionation studies to treatment and fate and effects evaluations.

MAJOR STUDY ELEMENTS

Literature Review. Literature was reviewed to identify relevant PCB and PAH characteristics and applicable sorption theory and research. Recent findings with respect to contaminant partitioning were reviewed and the implications and relevance to the present study assessed.

Size and Density Fractionation Study. Partitioning of PCBs and PAHs in sediments was assessed as a function of sediment composition. Operationally defined size and density fractions were isolated and analyzed for direct measurement of contaminants within those fractions and visualization of distribution trends. The importance of distribution trends to treatability using separation was evaluated.

Modeling. The relationship between contaminant concentration and sorptive phases was evaluated through regression of the fractionation data. A best-fit model was selected, and from this, phase specific distribution coefficients were developed. Overall findings were compared to those reported by other researchers and implications with respect to hydrophobicity, steric effects, competitive sorption and desorption resistance were discussed.

DOCUMENT ORGANIZATION

Previously Published Work. Chapters 2 through 4 of this paper present the results of earlier efforts to develop an approach for evaluating dredged material recovery potential. The work was motivated by a growing need for additional disposal space for sediments dredged in conjunction with maintenance of navigable waterways and an increasing awareness of dredged material as a potentially valuable resource. Principles of separation are introduced in Chapter 2. Methods for preliminary evaluation of material recovery potential were developed and are presented in Chapter 3. Chapter 4 discusses sediment-sampling principles and approaches relevant to potential material recovery assessments. All three of these chapters were previously published and are reproduced here with permission of the Engineering Research and Development Center (ERDC) Waterways Experiment Station. Other reports expanding on these topics have been published as well, including: "Physical separation (soil washing) equipment for volume reduction of contaminated soils and sediments" (Olin et al 1999), "Soil separation mobile treatment plant demonstration, Bayport confined disposal facility, Green Bay, Wisconsin" (Olin-Estes et al 2002a), "Planning level cost-benefit analysis for physical separation at confined disposal facilities" (Olin-Estes et al 2002b), and "Recovery of dredged material for beneficial use: the future role of physical separation processes" (Olin-Estes and Palermo 2001).

Each of these papers represents efforts to address gaps in the Corps of Engineers institutional knowledge with respect to necessary components of treatability studies, critical path inquiry in alternatives analysis, apriori assessment of process efficiency and benefit versus cost. Ultimately, all such evaluations should be grounded in the underlying science, and should facilitate decision-making in the field.

Present Study. Chapters 5 and 6 present the results of the fractionation study and some of the implications of the observed contaminant distribution. Chapter 7 presents the results of regression analysis on the fractionation data, by which phase specific contaminant concentrations were estimated. Phase specific distribution coefficients are developed in Chapters 8 and 9, and issues of labile/desorption resistant fractions and relative contribution to pore water concentrations are presented and discussed. Chapter 10 summarizes the work and discusses potential application and areas for further study.

BACKGROUND

PCBs. There is a significant body of research literature pertaining to the behavior and distribution of PCBs in the environment. PCBs were synthesized as early as 1881 and saw the beginning of widespread industrial applications around 1930 (Waid 1986). Environmental concerns about PCBs emerged in the mid 1960's, when accumulation of PCBs in fish and wildlife was first reported. Subsequent investigations revealed the widespread distribution of PCBs in the environment and in the food chain. The toxicity of PCBs came to light as a result of a tragic incident in Yusho, Japan, in which rice oil contaminated with PCBs was marketed and consumed by the populace over a period of several months, with catastrophic effects (Kuratsune et al.1972). Commercial production of PCBs ceased in the United States in 1977 (National Research Council 2001), but the environmental legacy of their uncontrolled use, management and disposal remains.

Chemically, PCBs are chlorinated, aromatic compounds. There are 209 congeners, containing from 1 to 10 chlorine (Cl) substituted on a biphenyl structure (monochlorobiphenyl to decachlorobiphenyl). Approximately 150 congeners are found in the environment (Hansen et al. 1999). PCBs are thermally stable and resistant to degradation by oxidation or chemical agents. PCBs also have excellent dielectric properties, which led to their widespread use as dielectric fluids in capacitors and transformers. They were also utilized as industrial fluids in various systems, in fire retardants, and in plasticizers used in adhesives, textiles, surface coatings, sealants, printing and copy paper (Hutzinger, Safe and Zitko 1983). Maximum annual U.S. production (peak 1970) was reported to be 39 million kg (85 million lb) (U.S. Department of Health and Human Services 2000).

PCBs are synthesized by a number of processes, including direct substitution on the preformed biphenyl system, phenylation of aromatic substrates, and other Aryl condensation reactions (Hutzinger, Safe and Zitko 1983). PCBs were generally marketed as mixtures, and these mixtures are commonly referred to as Aroclors, a Monsanto trade name. Other trade names include Clophen®, Phenoclor® and Pyralene®, Kaechlor®, Santotherm® and Fenclor®. Twelve different Aroclors with chlorine contents from 21 to 68% were produced in the U.S. (U.S. Department of Health and Human Services 2000). Aroclor® products are identified by a four-digit number (Hutzinger, Safe and Zitko 1983). The first two digits represent the type of molecule or the number of carbons in the biphenyl structure: 12=chlorinated biphenyl,

54=chlorinated terphenyl. (Terphenyl mixtures may contain biphenyls as well and are therefore also of interest). The last two digits represent the weight percent of chlorine. The most common Aroclors are Aroclor® 1242, 1248, 1254, and 1260 (Waid 1986). Others are Aroclor® 1016, 1221, 1232, 1262, and 1268. An exception to the nomenclature, Aroclor 1016 contains 41% chlorine, but with reduced penta-, hexa- and heptachlorobiphenyl content. Aroclor® 1254 "late" was produced in conjunction with Aroclor® 1016, 1016 being a distillate of the production process and 1254 a residual which was further chlorinated to achieve 54% chlorine. Aroclor mixtures may contain small amounts of polychlorinated dibenzofurans (PCDFs) as impurities (U.S. Department of Health and Human Services 2000). PCDFs are also formed during pyrolysis of PCBs. Aroclor® 1254 "late" contains increased levels of 2,3,7,8-tetrachlorodibenzo-p-dioxin, a compound having a high toxicity equivalency factor (TEF).

Aroclors range in appearance from a "clear, mobile oil" to a "light-yellow, soft, sticky resin". Reported specific gravity of Aroclors ranges from 1.182 to 1.811 (Hutzinger, Safe and Zitko 1983). Specific gravity of individual congeners is reported to range from approximately 0.98 to 1.51 (Mackay, Shiu and Ma 1992a). PCBs are highly lipophilic (fat soluble), but solubility in water is low, generally decreasing with increasing degree of chlorination. Reported congener solubility ranges from approximately 1.74E-07 to 7.8 mg/l at 25°C (Mackay, Shiu and Ma 1992a). The reported relative weight percent of the congeners present in each Aroclor (Waid 1986; U.S. Department of Health and Human Services 2000) are "representative" proportions, with some variability attributable to the manufacturing and purification processes, or, in the environment, to differential weathering of the various Aroclor components. Exact determination of the congener distribution is complicated analytically by the tendency for some congeners to co-elute.

PCBs have become distributed through the environment by a variety of mechanisms, including atmospheric and aquatic transport processes. Very high concentrations of PCBs have been found in the sediments of water bodies impacted by industrial outfalls and surface runoff from manufacturing facilities. In the environment, major transport mechanisms are volatilization and redeposition, bioaccumulation and biomagnification, biotransformation/biodegradation, and particulate facilitated transport. Because of the low solubility of PCBs, transport in the aqueous phase is perhaps less significant, although important to uptake by aquatic organisms. Measured solubility of PCB Aroclors is actually representative of the more water-soluble congeners making up the mixture. These congeners are typically those with lower molecular weight (lower Cl content), which are also more volatile (Luthy et al. 1997). Congeners of higher molecular weight tend to be associated with mineral and organic particulates in the environment, with organic sorption dominating (Girvin and Scott 1997; Karichoff 1984), although the presence of high levels of dissolved organic carbon (actually a filterable colloidal phase) can increase the apparent solubility of these congeners (Brannon et al. 1998; Hwang et al. 1998).

The 2-stage sorption of PCBs reported by various researchers is thought to be indicative of the initial sorption of smaller, more soluble congeners followed by sorption of larger, more hydrophobic congeners, whose sorption is retarded because of low solubility and steric effects (Gong et al. 1998; Girvin and Scott 1997). Parameters that may influence rate and possibly location of congener sorption include molecular size, configuration (planar versus non-planar), location of Cl substitutions, and polarity. Of the 209 possible PCB congners, 68 are co-planar (EPA 2004). These are PCBs with either no chlorine substitutions in the ortho position (CP0) or one chlorine in the ortho position (CP1), which allows both benzene rings to rotate into the same plane. Planar configuration reduces steric effects in sorption processes. In several recent

studies, Cornelissen et al. (2004), Jonker and Koelmans (2002) and Bucheli and Gustafsson (2000) demonstrated that sorption to black carbon is stronger for planar PCBs than for non-planar PCBs due to steric effects.

PAHs. PAHs are ubiquitous compounds, loosely categorized as either petrogenic or pyrogenic in origin, although there is some overlap between categories. There is a third source category, biogenic, not often mentioned in the sorption literature. Biogenic PAHs are formed from natural biological processes including diagenesis (Thorsen, Cope and Shea 2004). Pyrogenic PAHs (such as anthracene and benzo[a]pyrene) are generated as a byproduct of incomplete combustion of organic materials, such as fossil fuels, wood, coal, or even charbroiled meat. Coking facilities, where coal is burned to produce coke for fueling blast furnaces, are historically associated with high levels of PAH contamination. Petrogenic PAHs (such as naphthalenes, fluorenes, phenanthrenes, dibenzothiophenes, and chrysenes) are derived from petroleum and may be introduced to the environment in a co-solvent such as crude oil (Thorsen, Cope and Shea 2004). PAHs are produced commercially and are found in a variety of products including coal tar, crude oil, creosote, roofing tar, and even some medicines, dyes, plastics and pesticides.

PAHs comprise of a group of approximately 100 heterogeneous compounds. Structurally, PAHs are composed of three or more benzene rings, at least two of which are fused with two neighboring rings sharing two adjacent carbon atoms (ToxProbe Inc. 2002). PAHs may be composed of carbon and hydrogen only or may contain substitutions, such as nitrogen and sulphur. Petrogenic (petroleum) PAHs are dominated by low molecular-weight compounds, and have a greater abundance of methylated derivatives than parent compounds. Pyrogenic PAHs are typified by high molecular-weight compounds (more than 4 rings) with parent PAHs more abundant than methylated compounds (Depree et al. 2004). Ratios of specific compounds may be helpful in determining PAH source. Gustafsson and Gschwend (1997) assembled source-diagnostic ratios from a large literature data set. Values less than one for two specific ratios (sum of methyl-phenanthrenes and anthracenes to phenanthrene and methyl-pyrenes and fluoranthenes to pyrene) are indicative of pyrogenic sources. These ratios have values near 5 and 4, respectively, for petrogenic sources.

In their pure form, PAHs are colorless, white, or pale yellow-green solids. PAHs have comparable solubility and octanol-water coefficients to PCBs (Müller et al. 2000). Reported solubility of the most common PAHs range from 2.6E-04 mg/L (Benzo [g,h,i] perylene at 25ºC) to 3.93 mg/L (Acenapthene), with solubility decreasing with increasing molecular weight. For the same group of PAHs, temperature dependent specific gravity ranges from 0.8988 to 1.283 (ToxProbe Inc. 2002).

Atmospheric deposition is a major transport mechanism for PAHs. Because PAHs are relatively insoluble, in soils and sediments they are typically associated with particulates, humic matter, or dissolved in oily matter (ToxProbe Inc. 2002). Sorption to organic matter appears to be even more significant for PAHs than for PCBs (Chiou, McGroddy and Kile 1998). This is attributed to a high affinity for the aromatic structures in organic matter (Chiou, McGroddy and Kile 1998) and the planar configuration of PAHs, which reduces steric effects (Gauthier et al. 1987; Chin et al. 1997 as cited in Müller et al. 2000; Cornelissen et al. 2004). PAHs have a high affinity for soot, and pyrogenic PAHs may be co-produced with (a component of) soot. However, DOC composed of aliphatic carbon (non-aromatic) has been shown to be less important than soil organic matter and clays in sorption of PAHs (Hwang and Cutright 2004).

Although environmental levels of PAHs are typically not toxic, PAHs can induce toxic effects. Some PAHs are carcinogenic, and genotoxicity (potential for damaging DNA) has been demonstrated. The most toxic PAHs contain four to seven rings. PAHs are thought to be carcinogenic, although human research data appears to be limited. Like PCBs, PAHs are highly fat-soluble. Because they are lipophilic, bioaccumulation is a concern. PAHs are subject to photo-oxidation and biodegradation (ToxProbe Inc. 2002).

Soot Composition. Strictly speaking, soot is an operationally defined fraction of a continuum. The portion of the continuum that can be isolated is the portion that lends itself to study generally. The physico-chemical characteristics of the separable fraction may still vary widely. Black carbon is typically isolated from other forms of organic carbon by chemical or thermal (375º C) oxidation to remove amorphous organic carbon, followed by acidification to remove most mineral matter (Cornelissen et al. 2004). Limitations to these methods include artifactual formation of black carbon as a result of charring of high nitrogen content particles and loss of less-condensed soot fractions. Low black carbon:organic carbon ratios typify a good separation. The soot fraction is typically within 2-30% of total organic carbon in coastal sediments (Gustafsson and Gschwend 1998, Masiello and Druffel 1998 and Middleburg et al. 1999, all as cited in Bucheli and Gustafsson 2000). The diameter of soot particles may span several orders of magnitude (Gustafsson and Gschwend 1997), including individual coarse charcoal particles (few to tens of μm in size) found in sediments and fine soot particles (3-30 nm in diameter), typically aggregated in grape like clusters formed from vapor phase processes. Densities range from 1.8 to 2.1 g/cm^3, as compared to pure graphite (2.1-2.2 g/cm^3) (Risby and Sehnert 1988; Ross et al. 1982, both as cited in Gustafsson and Gschwend 1997). Gustafsson and Gschwend (1997) report Brunauer-Emmet-Teller (BET) surface area of approximately 100 m^2/g, assuming the given density range. Cornelissen et al. (2004) estimated nanopore surface area of 58 m^2/g, using low nitrogen pressures and the DFT model (Lastoskie and Gubbins 2000 as cited in Cornelissen et al. 2004). Further, Cornelissen et al (2004) estimated that the size of black carbon nano-pores were in the range of <4-10Å, as compared to clay mineral silicate pores (10-20 Å) and other oxide minerals (>25 Å).

Gustafsson and Gschwend (1997) describe soot as a multi-layered aromatic system, with large carbon:hydrogen and carbon:oxygen elemental ratios suggesting a highly condensed and conjugated structure, that is 90-100% aromatic (Hamins 1993 and Akhter et al. 1985, as cited in Gustafsson and Gschwend 1997). "Soot may be thought of as particles of multi-layered macro PAHs (conjugated blocks of about 30 rings) structurally held together with some carbon-bridges and ether-linkages, and containing some substitution of conjugated carbonyls and acid anhydrides" (Gustafsson and Gschwend 1997). Given such a description, PAHs must be correlated to soot content. This suggests that discrimination between "structural" PAH (soot) and anthropogenic PAH is an important aspect of sorption analysis. Jonker and Koelmans (2002) approach this by providing values for both native PAH and added PAH in reporting sorption study results. It is not entirely clear, however, whether the term "native PAH" distinguishes between both strongly sorbed PAH present in-situ and structural PAH.

Sorption Theory. Adsorption is a surface phenomenon, involving a heterogeneous system composed of a fluid phase and a solid surface. A species is considered adsorbed on the solid surface if the concentration of the species in the fluid-solid boundary region is higher than

that in the bulk of the fluid (Tien 1994). The maximum extent of adsorption is more a function of diffusion and equilibrium than solubility. Mechanisms of sorption include interaction by London-van der Waals forces, precipitation on the solid surface, ion exchange, chemisorption, and binding of sorbate complexes. Adsorption can occur on the external and internal surfaces of the sorbent; a good sorbent will have a high surface area per unit mass. Sorption behavior is typically described using an isotherm, a graphical representation of sorbed contaminant concentration to fluid phase contaminant concentration.

Adsorption of organic substances from liquid solutions can be treated analogous to gas adsorption, for which various isotherm expressions have been developed (Tien 1994). Based on analysis by other researchers (Hansen et al 1999; EPA 1999; Girvin and Scott 1997), at dilute concentrations, soil-water partitioning of hydrophobic compounds such as PCBs is generally well represented using a linear (or linear Freundlich) isotherm:

$$q = Kc^{1/n} \tag{1-1}$$

where

q = mass sorbate adsorbed per unit mass sorbent, mg/kg
c = concentration of sorbate in aqueous solution, mg/L
n = empirical exponent, =1 for linear form
K = distribution coefficient, L/kg, which by inference is defined as:

$$K_d = \frac{q}{c} = \frac{C_s}{C_w} \tag{1-2}$$

where, at equilibrium

C_s = concentration of sorbate adsorbed, mg/kg
C_w = concentration of sorbate in aqueous phase, mg/L

Kohl and Rice (1999), however, reported non-linear adsorption of PAHs, which was best represented by the Freundlich equation with 1/n less than 1.

The K_d model derives from thermodynamic chemistry (EPA 1999), in which the following assumptions are made: unoccupied surface adsorption sites are much greater than the total dissolved sorbate remaining in solution at equilibrium, the activity of the sorbate on the solid at equilibrium is equal to 1, the system is reversible and independent of the sorbate concentration in the aqueous phase, and the system is precisely described, with fixed pH and temperature, one type of adsorption site, and one type of dissolved aqueous species. Several of these assumptions are violated in modeling a sediment/water system, but for saturated conditions and non-polar organic constituents at dilute concentrations, the K_d model performs relatively well, although resulting distribution coefficients are highly site specific.

There are a number of methods for determining K_d values (EPA 1999), including:

- Laboratory batch studies
- In-situ batch studies
- K_{oc} method

Values obtained by different methods may vary by over an order of magnitude. From batch studies using a known mass of sediment (M_{sed}) and volume water (V_w) at a specified initial concentration (C_o), K_d is given by:

$$K_d = \frac{V_w(C_o - C_i)}{M_{sed} C_i} \quad (1\text{-}3)$$

where

C_i = concentration of sorbate in solution at equilibrium, mg/L

Batch studies do not differentiate between sorption mechanisms, and K_d will also include degradation for organic compounds subject to breakdown under testing conditions. A variation on the batch method is to conduct a series of tests varying only the initial concentration of the sorbate in solution (C_o). The K_d for the resulting isotherm is the slope of C_i versus q.

In addition to violating the assumptions of the thermodynamic K_d, variation in K_d values obtained using the batch method may be introduced by differences in experimental method and temperature (EPA 1999). Additionally, if multiple species of a constituent are present in solution, the resulting K_d will represent a composite of these species. However, the batch K_d is generally accepted if the system is well represented by the soil or sediment and water used for testing.

K_d is estimated from insitu batch studies by separating the solid and aqueous phases of a field sample and directly measuring sorbed and dissolved concentrations of the sorbate. The assumption of equilibrium is more likely met using this method, and artifacts associated with batch testing are largely eliminated.

The K_{oc} method assumes hydrophobic organic compounds sorb preferentially to natural organic matter (EPA 1999). A distribution coefficient is defined as follows:

$$K_d = K_{oc} f_{oc} \quad (1\text{-}4)$$

where

K_{oc} = ratio of the contaminant concentration on the organic matter on a dry weight basis to dissolved concentration in the surrounding fluid, L/kg

f_{oc} = fraction of organic carbon in the soil, unitless

Organic carbon partitioning coefficients are typically constant over a range of environmental and experimental conditions (EPA 1999), although probably inapplicable under the following conditions:

- f_{oc} <lower threshold value (reference values from 0.1 percent to a few percent, with 1.0 percent cited in EPA 1999)
- f_{oc} >upper threshold value (20 percent, EPA 1988, as cited in EPA 1999)
- There is a large expandable clay component (a competing fraction)

- Partitioning organic compound is polar
- Ion exchange is sorption mechanism
- Time to equilibrium is lengthy
- DOC (colloidal) bound sorbate in the dissolved phase

K_{oc} has been extensively correlated to the octanol-water partition coefficient K_{ow} for a number of compounds (EPA 1999):

$$K_{oc} = \alpha K_{ow} \qquad (1\text{-}5)$$

where

α = correlation coefficient, unitless, with values reported in the literature ranging from 0.25 to approximately 1.0

Because of the practical problems associated with the determination of K_{ow} and K_d for PCB congeners, Hansen et al. (1999) developed another approach to estimating K_d, using the relative (gas chromatograph) retention time (RRT) and molecular surface area (TSA) of the sorbate to estimate log K_{oc} and log K_{ow}. The approach was applied for all 209 congeners and predicted values of K_{ow} and K_d compared to experimental values from carefully selected datasets. Because the composition of organic matter in soils is spatially variable and dynamic, due to biological breakdown, Hansen et al. (1999) also proposes a non-linear correlation between f_{oc} <lower threshold value, K_d and f_{oc}:

$$K_{oc} = K_d / (f_{oc})^n \qquad (1\text{-}6)$$

where f_{oc} reference values range from 0.1 percent to a few percent, with 1.0 percent cited in EPA 1999, and n has values less than one, reportedly ranging from 0.6-0.8.

Values of K_{oc} were calculated (Hansen et al. 1999) for measured K_d and f_{oc}, assuming a value for n of 0.7 in Equation 1-6. These values were plotted against RRT and TSA and regression equations were developed to generate predicted K_{oc} values based on RRT and TSA. The predicted K_{oc} values compared favorably to an independent experimental data set, as did predicted K_{ow} and K_d values obtained by plotting experimental data against RRT and TSA. Error for the regression equations was reduced by grouping the PCB data according to ortho and meta substitution, suggesting that the planar assumption inherent in similar correlations developed by Hawker and Connel (1988, as cited in Hansen et al. 1999) is fundamentally insufficient to describe PCBs sorption. Hansen et al. (1999) suggest that lack of precision in published experimental values for log K_{ow} may be responsible for the failure of predictive equations for compounds having log K_{ow} above 5.5 or 6. The predicted K_{ow} developed using this method could possibly also be used to calculate more accurate K_{oc} values for all congeners using the correlation described by Equation 1-5, but this was not addressed.

An additional consideration in the development of K_{oc} values is the composition of organic matter. Hansen et al. (1999) alludes to this in proposing a non-linear relationship between K_d and f_{oc} (Equation 1-6). Soot has been demonstrated to have a high affinity for organic contaminants (Gustafsson et al. 2002; Lohmann, MacFarlane and Gschwend 2002).

Brannon et al. (1998) demonstrated a correlation of K_{oc} to aromaticity of sediment organic matter.

In Brannon et al. (1998), a dissolved organic carbon (DOC) partitioning coefficient (K_{DOC}) was calculated from a regression of sorbed (normalized to DOC concentrations) versus truly dissolved PCB concentrations for humic acid isolates in water. Results suggest that sediment humic acid may be more aromatic in character than humic acids isolated from soils and water, with attendant K_{oc} values for nonpolar organic contaminants in sediments greater than that of soils. Partitioning of a hydrophobic organic compound between dissolved organic carbon (DOC) and water at equilibrium is given by:

$$K_{DOC} = C_{DOC} / C_w \qquad (1\text{-}7)$$

where

C_{DOC} = concentration of contaminant sorbed to the dissolved organic carbon, mg/kg
C_W = truly dissolved aqueous phase contaminant concentration, mg/L

Chiou, McGroddy and Kile (1998) also noted the importance of the aromaticity of organic matter to the sorption of PAHs. Chiou et al. (1983) gives the following relationships between K_{oc} and K_{ow} for PCBs and PAHs, respectively, suggesting higher sorption of PAHs for similar octanol-water coefficients:

$$\log K_{OC} = 0.904 \log K_{OW} - 0.543 \qquad (1\text{-}8)$$

$$\log K_{OC} = 1.00 \log K_{OW} - 0.21 \qquad (1\text{-}9)$$

The similarity of Equation 1-7 to the equation for the solids distribution coefficient (Equation 1-2) is quite evident. DOC is, in fact, operationally defined by filter size. For organic compounds, this is typically 0.7 μm. DOC is then potentially a colloidal solid phase, and sorption behavior may reasonably be described by the same parameters as the soil or sediment solids. In calculating K_d from experimental data, an important implication of the Brannon et al. (1998) study is the need to account for sorption to DOC. This is addressed in DiToro et al. (1991) as follows:

$$K_{d'} = \frac{f_{oc} K_{oc}}{1 + K_{oc} DOC \quad 10^{-6}} \qquad (1\text{-}10)$$

where

$K_{d'}$ = apparent distribution coefficient
DOC = dissolved organic carbon concentration, mg/L

A study conducted by Pardue et al. (1993) further illustrates the importance of DOC as a third phase, comparing observed distribution coefficients for a high organic marsh soil and a

mineral dominated bottomland hardwood soil. The organic marsh soil evidenced a lower distribution coefficient, attributed to the influence of DOC and the association of the contaminants with that phase. Pardue et al. (1993) gives the following relationship for the apparent distribution coefficient:

$$K_{p-obs} = \frac{K_p}{(1 + (K_{DOC} C_{DOC} / 10^6))} \tag{1-11}$$

Using a combination of the K_{oc} model and a parametric model, Strenge and Peterson (1989) estimated partition coefficients for organic compounds on soils (EPA 1999). Parametric models are simply regressions on data obtained by varying the value of independent variables, typically using a factorial experimental design. Based on the concentrations of organic material (C_{om}, percent by weight), clay (C_{clay}, percent by weight), silt (C_{silt}, percent by weight) and sand (C_{sand}, percent by weight) they obtained:

$$K_d = 10^{-4} K_{oc} \left[57.735(C_{om}) + 2.0(C_{clay}) + 0.4(C_{silt}) + 0.005(C_{sand}) \right] \tag{1-12}$$

These studies illustrate that there are any number of soil and sediment parameters that might be treated as separate phases and utilized to develop and improve predictive equations for contaminant partitioning. Further, co-contaminants, such as oil and grease, might also be treated as a separate phase and factors introduced to account for partitioning to this phase.

It has been observed that measured distribution coefficients often do not correspond well to coefficients predicted using K_{OC}/K_{OW} relationships (Kan et al. 1998). Aqueous concentrations are generally overpredicted, suggesting that desorption is not occurring as completely or as rapidly as expected. This is born out by the sorption-desorption hysteresis observed in many sorption studies. Mechanisms that have been proposed to explain resistant desorption include chemisorption, heterogeneous sorption sites, diffusion limitations and irreversible sorption (Kan et al. 1998; Kan et al. 1994; Hatzinger and Alexander 1995). The two-stage sorption that is observed for hydrophobic organic compounds, attributed to low solubility and steric effects, may also be evident in retarded desorption from soil micropores. Hatzinger and Alexander (1995) describe the increasing desorption resistance of chemicals with time as chemical aging (distinct from reactions altering the structure of the compound, such as covalent bonding). Hatzinger and Alexander (1995) demonstrated that diffusion limitations do play a role in desorption resistance, but are not necessarily solely responsible. Kan et al. (1998) observed that there was a component of irreversible sorption for each of three sediments studied and proposed a two-phase sorption model to describe reversible and irreversible components. Research has also focused on the existence of organic matter domains. Young, amorphous organic material demonstrates different sorption properties than more condensed or glassy forms such as soot, which has high specificity for organic contaminants (Karapanagioti et al. 2000, Kan et al. 1998). Huang and Weber (1997) evaluated the elemental composition of several soils and sediments of different age and diagenetic history, observing that K_{OC} increased with increasing age of the materials as measured by the O/C atomic ratio. A study by Karapanagioti et al. (2000) examined the influence of heterogeneous organic matter on sorption, attributing non-linear sorption behavior to the presence of condensed forms, including coal and soot containing phases. Bucheli and Gustafsson (2000) measured soot distribution coefficients for several PAHs approximately 2

orders of magnitude higher than those predicted by K_{OC}/K_{OW} relationships. Bucheli and Gustafsson (2000) also compared the distribution coefficients they obtained for soot to those obtained for tertiary lignite and bituminous shale. Surface normalized coefficients were slightly higher for lignite and shale, but specific surface area of these materials is lower than for soot. Therefore, they are likely to have less overall impact on a mass basis. In summary, both the age and the degree of condensation of the organic material, as well as the length of time the contaminant has been in contact with the material, appear to play a very important role in contaminant partitioning and subsequent transport and bioavailability.

PROBLEM STATEMENT

Contaminant distribution is integral to environmental evaluations of contaminated sediment on every level. The technical and economic feasibility of treatment or beneficial use is a function of the accessibility or separability of the contaminants within the sediment. The magnitude of release to the environment during dredging and disposal is dependent upon the partitioning behavior of the contaminants. Meaningful risk assessment is contingent upon making reasonable predictions of the magnitude of exposure of target organisms. For some exposure routes, such as ingestion, contaminant concentration in a specific particle size fraction may be particularly relevant.

Despite the fact that the importance of contaminant distribution is recognized, to some extent, the topic has been approached in a broad-brush fashion. Most contaminant distribution studies treat particles smaller than 63-75μm as a single fraction. There is little published specific to evaluating the magnitude of contaminant enrichment in the <5 μm fraction. Distribution studies correlating contaminant concentration to percent expandable clay or to fraction organic carbon are site-specific evaluations. Further, correlations are established on the basis of the proportional sediment composition and bulk sediment concentration, rather than direct measurement of the separate fractions. In part, this may be attributable to the difficulty of making effective separations involving fine particles. However, even imperfect separations provide comparative information useful in establishing correlations to various sediment constituents, and may offer improved estimates of the role of the different fractions in sorption over data obtained from bulk sediment alone.

With respect to PCBs, there appear to be few experimentally obtained congener specific values for K_{oc}, and most of the experimental values reported in the literature cited were obtained by normalizing K_d with the organic carbon fraction, rather than direct measurement of the sediment organic fraction (100% preferential distribution to the organic fraction was assumed). Similarly, the majority of K_{oc} values reported for PAHs in the comprehensive reference by Mackay, Shiu and Ma (1992b) were calculated from the octanol-water coefficient. Preliminary fractionation studies indicate that organic carbon is not always correlated with the highest contaminant concentrations, however, implying the presence of other fractions with an equal or greater role in the sorption of hydrophobic contaminants. Data obtained to date suggest that in some cases soot may be a more appropriate normalizing parameter than organic carbon. Oil and grease also appears to be a very important phase.

Conventional methods of deriving distribution coefficients, whether theoretical or site-specific, provide little information regarding the relative contaminant loading of each of the sorptive phases. Distribution coefficients may be normalized to organic carbon, but organic carbon itself may be composed of multiple phases. Oil and grease, soot and organic carbon all

comprise a portion of the total organic carbon (TOC) measurement, yet bioavailability of contaminants in these phases may be vastly different. The ultimate disposition of each of these phases as a consequence of treatment may also be different and may determine the effectiveness of treatment. This study was focused on the relative distribution of PAHs and PCBs in the size and density fractions of selected sediments, which were physically separated for direct measurement and evaluation of the distribution of contaminants and correspondence to distribution of sorptive phases.

APPROACH

Method Development. Customarily, the potential impacts of dredging and disposal actions on the environment have been evaluated based upon bulk sediment chemistry. Beneficial use evaluations have focused almost exclusively on recovering the sand fraction, which was presumed "clean". Fine materials were assumed to be more contaminated and, when they were evaluated, were aggregated together for assessment and testing. Intuitively, however, a definitive contaminant distribution would be expected within the fine fractions, attributable to differences in particle size and mineralogy. Further, organic or carbonaceous materials with a high affinity for contaminants may potentially be found in any size fraction. Bench scale testing protocols were therefore needed to enable the prediction of contaminant loading in operationally important sediment fractions, those fractions representative of the separations that would occur using various field separation processes. Bench and field research has been conducted to develop a streamlined testing methodology, identify testing artifacts, and to validate bench scale results at field scale.

The operationally defined fractions were determined based on the outcome of previous distribution studies and the expected mineralogical composition of the different size fractions. Sand and silt size minerals (particles approximately 3-5 μm up to 4.75 mm) are largely physical weathering products of primary minerals, having similar mineralogical composition and surface reactivity. Clays (roughly particles <3-5 μm in size) are chemical weathering products of primary minerals, characterized by high surface area and unique structures responsible for their documented potential as sorbents and ion exchange media. Based on these considerations and results obtained in previous studies, there appear to be three size fractions that are of primary interest in terms of the information that can be derived from them and their relevance to practical applications: sand (0.075-4.75 mm), silt (0.005-0.075 mm) and clay (<0.005 mm).

Mineral and organic fractions are also expected to have different affinity for contaminants. These fractions may be separated based on density differences. Composition of organic material varies, but most references place the density of organic material at less than 1.8 g/cm^3. Initial studies utilized a separation at 1.8 g/cm^3. This was later increased to 2.0 g/cm^3, which qualitatively appeared to produce two distinct fractions with little or no carryover of organic material into the "mineral fraction". (Given reported specific gravity values for soot (Risby and Sehnert 1988; Ross et al. 1982, both as cited in Gustafsson and Gschwend 1997), separation at 2.1 g/cm^3 might further improve the separation of carbon based materials and minerals.)

Regardless of the separation process employed, most do not produce a pure size or density fraction. It was therefore decided that the most useful (and repeatable) size separation would be one that was representative of that attainable in the field. A 2" hydrocyclone was subsequently employed to separate the silt and clay fractions of the three sediments studied.

Since hydrocyclones produce a distribution around the cut size, the resulting fractions are enriched in silt or clay, but are not pure fractions. They are indicative of the contaminant reduction that might be achieved in the fine fraction, however, by reducing the clay content. The selected operationally defined fractions were as follows:

- Sand, separated by sieving (75µm-4.75 mm)
- Silt, 2" hydrocyclone underflow (<75 µm)
- Clay, 2" hydrocyclone overflow (<75 µm)
- Organic, materials with specific gravity <2.0
- Mineral, materials with specific gravity >2.0

Oil and grease, soot, and clay were all identified as potentially important sorptive phases based on contaminant distribution observed in previous soil and sediment studies conducted at ERDC and by others. Figure 1-1 illustrates the potential importance of clay size fractions to organic contaminant distribution, although this may be attributable to the abundance of TOC in the clay size fraction, rather than the structure and surface area of the clay minerals. Figures 1-2 and 1-3 illustrate contaminant distribution for bulk sediment, two density fractions and two size fractions, influenced more by O&G than by TOC or size fraction.

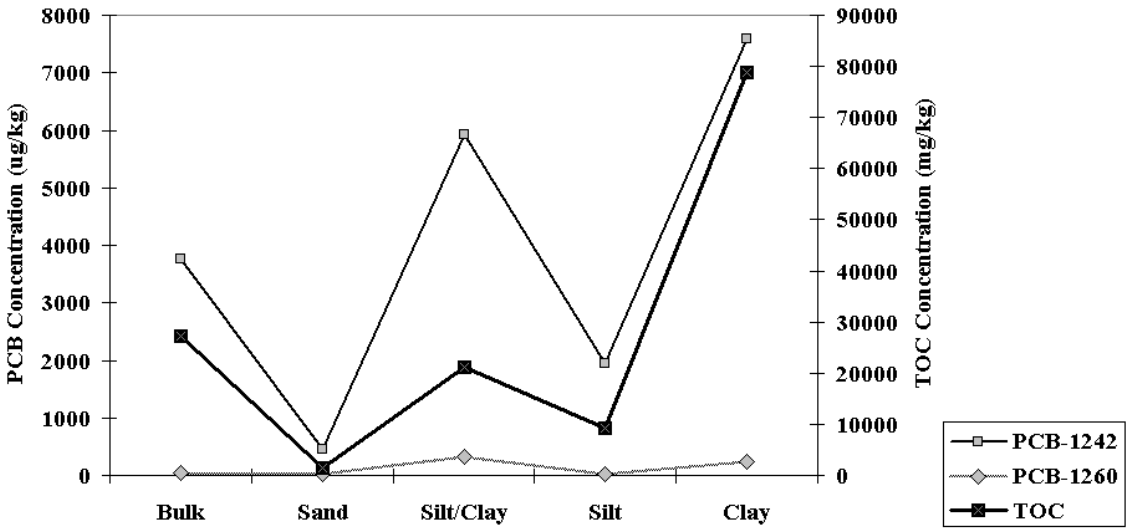

FIGURE 1-1. Contaminant enrichment in clay size fraction for a freshwater sediment.

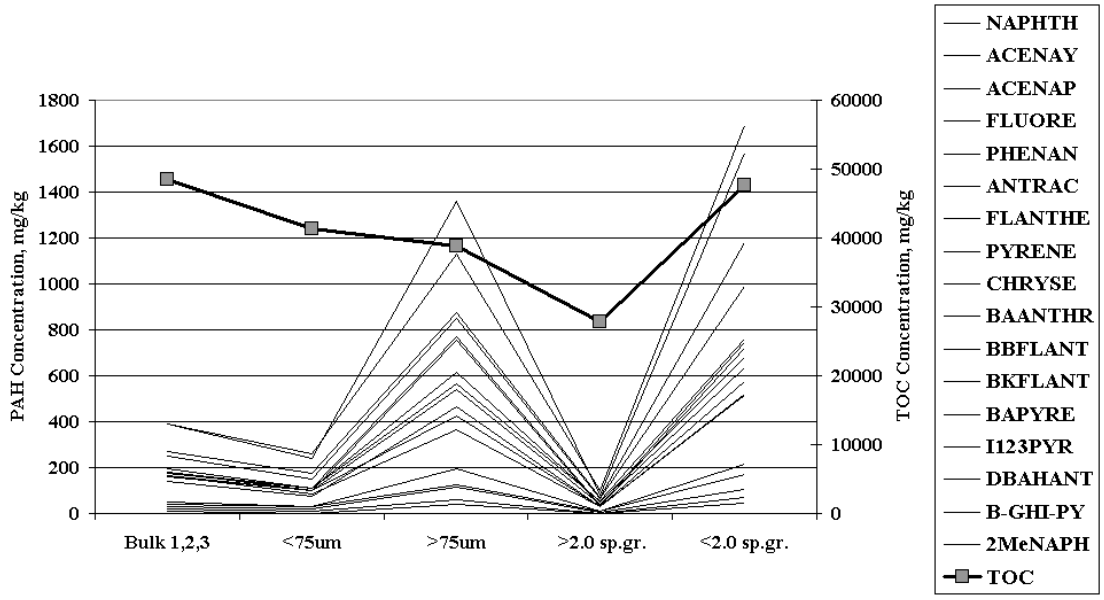

FIGURE 1-2. PAH distribution relative to TOC distribution in bulk sediment, size and density fractions for a freshwater sediment.

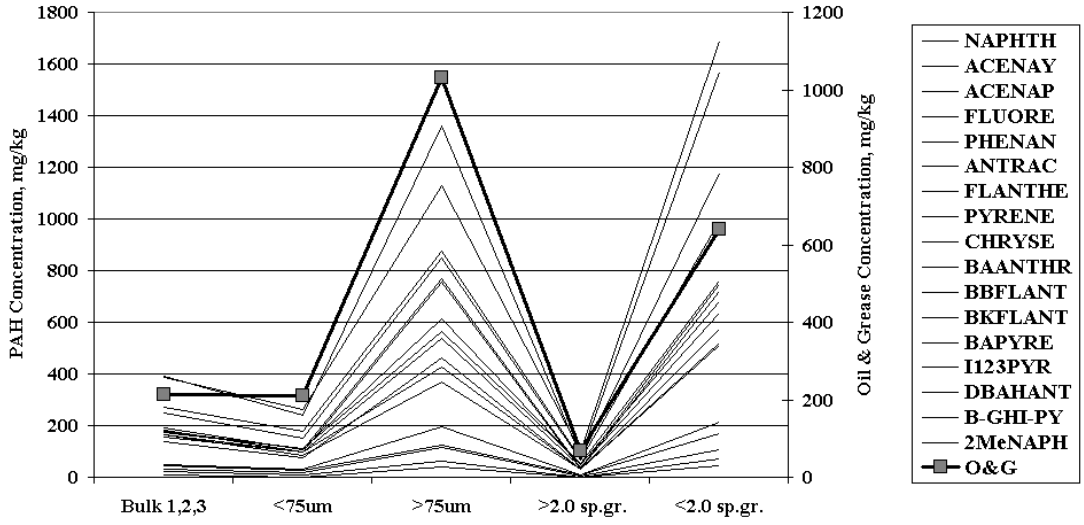

FIGURE 1-3. PAH distribution with respect to O&G in bulk sediment, size and density fractions for a freshwater sediment.

Present Study. Direct measurement of contaminant concentrations in sorptive phases is not practical due to the difficulty of separating the sorptive phases in quantities sufficient for analysis and without destroying the compounds of interest. Fractionation studies were therefore conducted to obtain differential measurements of contaminants and sorptive phases in operationally defined fractions of three natural sediments: two marine and one freshwater. Sediments from locations with an established history of PCB and PAH contamination were selected for this study[1].

The homogenized bulk sediments were first characterized with respect to particle size, density, organic content and other relevant parameters. The bulk sediment, operationally defined sediment fractions as previously defined, and the pore water, were analyzed for a suite of contaminants including 70 PCB congeners, 17 PAHs, total organic carbon, soot, and oil and grease. PCB congeners were selected from a group inclusive of the components of the most common Aroclor mixtures and each of the homolog groups, taking into consideration the tendency of some congeners to co-elute. PAHs represent compounds that are commonly found in navigation sediments and represent a fairly standard list of analytes in dredged material assessment.

Separation procedures and resulting contaminant distribution are more fully described in Chapters 5 (PAHs) and 6 (PCBs). Four models were proposed to describe the distribution of contaminants among the sorptive phases. Two were linear combinations of the sorptive phase mass (soot, organic carbon and oil and grease), with and without the clay fraction. Two were non-linear, with and without the clay fraction. Parametric and non-parametric statistical procedures were used as appropriate in model development and to establish correlations between contaminant and sorptive phases for the selected model. Based on the regressions, contaminant concentrations in each of the sorptive phases could be estimated. These procedures and the results of the regressions are fully described for both contaminant groups in Chapter 7. The phase specific contaminant concentrations obtained by regression on the fractionation data were then utilized to develop phase specific distribution coefficients. For comparison, this was done first by assuming each sorptive phase to be in equilibrium to the pore water at the measured concentration, and then by apportioning the pore water concentration between the phases, based on measurement of a desorption resistant fraction. The results of that comparison raise some interesting questions with respect to the location of the desorption-resistant fraction. The desorption study and procedures used in calculation of the phase specific distribution coefficients are fully described for both PAHs and PCBs in Chapter 8.

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[1] The study samples were taken from well-known harbors with the specific objective of obtaining materials containing sufficient contaminant levels to facilitate testing. They were obtained as grab samples from a single location or limited area and do not necessarily represent the character of the materials in these water bodies as a whole.

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CHAPTER 2

DETERMINING RECOVERY POTENTIAL OF DREDGED MATERIAL FOR BENEFICIAL USE – SOIL SEPARATION CONCEPTS[1]

BACKGROUND

Contaminated dredged material is often placed in confined disposal facilities (CDFs), but as land development and acquisition costs continue to rise, there is a growing shortage of CDF storage capacity. Several options can be considered to increase capacity, including restricted disposal (that is, storage of only the most contaminated sediments), dredged material dewatering and densification, and, more recently, reclamation and reuse of materials from the CDF. Physical separation (soil washing) is a management approach that has been applied at several projects and holds promise as a potentially low-cost method to recover materials for beneficial use (BU) and to restore CDF capacity.

Physical separation or soil washing in this context refers to the process of classifying or separating sediment into fractions according to particle size or density. Separation may be accomplished by screening, gravity settling, flotation, or hydraulic classification, using devices such as hydrocyclones (Averett et al. 1990; Allen 1994; U.S. Environmental Protection Agency (USEPA) 1994b; Olin et al. 1999). Equipment for physical separation is widely available and the concept has been demonstrated for sediments in both the United States and Europe (USEPA 1994a; Zwakhals, Deibel and van Rijt 1995; Detzner, Kitschen and Weimerskirch 1995; Granat 1998). Additionally, various site design and operational approaches can also be effective in achieving separation during placement of dredged material in a conventional CDF (Olin and Bowman 1996; Zwakhals, Deibel and van Rijt 1995). However, methods to evaluate the feasibility of separation for a given dredged material or for a given CDF site, considering environmental, logistical, and economic factors, are not yet well established (Olin and Bowman 1996).

The feasibility of separation as a management approach is dependent on several factors, including: 1) ability to identify distinct fractions within the material meeting BU criteria, 2) ability to separate suitable fractions, and 3) material recovery potential (MRP) as determined by available volumes of suitable material. This chapter introduces the technical considerations of physical separation as applied to dredged material and provides a framework for evaluation of physical separation. Olin-Estes (2000) and Olin-Estes and Palermo (2000) address data acquisition and utilization for evaluating MRP. The information contained in those articles is applicable to MRP determination, not only for physical separation feasibility evaluation but also for beneficial use recovery in general.

INTRODUCTION

An overall approach to evaluate feasibility of separation as a management option is illustrated in the flowchart (Figure 2-1). The need for recovery or preservation of CDF capacity

[1] Reproduced with permission from the U.S. Army Engineer Research and Development Center (ERDC), Vicksburg, Mississippi.

should first be evaluated based on available capacity and projected future needs, although adequate long-term capacity need not rule out beneficial use of dredged material. A screening examination of proposed beneficial use applications for the locale should be conducted to determine if the material can be used without pretreatment. If available information is inadequate, at least limited sampling of the material will be needed to make a preliminary determination. Preliminary sampling and data acquisition is further discussed in Olin-Estes and Palermo (2000). If separation appears to be necessary to meet material specifications for identified beneficial uses, an evaluation of material recovery potential and a more detailed sediment/site characterization and evaluation is needed. Extensive site sampling and data interpretation is further discussed in Olin-Estes (2000). Material characterization, physical separation processes and limitations, and determination of MRP are discussed in the following sections.

MATERIAL CHARACTERIZATION

Material characterization is necessary both to determine "as is" suitability of material for BU and, when found not suitable, to determine feasibility of physical separation for recovering usable fractions. Preliminary material characterization for BU screening purposes generally includes a particle size distribution analysis and bulk (unseparated) chemical contaminant analysis, since acceptable grain size and contaminant levels are specified for most, if not all, beneficial uses. Other parameters may also be of interest, depending upon the BU specifications, but might include clay content, liquid limit, plastic limit and moisture content.

If bulk material is found to be unsuitable as is for identified BU, a more comprehensive characterization is required. This typically implies a contaminant distribution, or fractionation, analysis in which material is separated into different size and density fractions. Fractionation studies permit evaluation of the quality of the respective size and density fractions of the material under consideration. Anecdotal evidence suggests that separation of sandy materials results in a large proportion of contaminants of concern (COC) remaining associated with the fine silt and clay fraction (Allen 1994; Olin and Bowman 1996; Olin et al. 1999). Although coarse minerals, sand size and larger, are typically relatively uncontaminated, in some cases efficient separation of coarse and fine fractions may be difficult. A clean coarse product will therefore be difficult to produce, or may require additional processing operations.

Organic materials of all sizes will typically have higher contaminant levels than any of the mineral fractions, including the clays, particularly for hydrophobic organic contaminants. The contribution of organic material to overall contaminant levels can be determined from a density fractionation study. Collectively, contaminant distribution information is used to determine whether or not an acceptable size or density fraction is likely to be recoverable from the material, what percentage of the material this represents, and what unit operations are likely to be needed to achieve this separation. Organically bound contaminants may be less available than mineralogically bound contaminants. Bioavailability may ultimately determine whether this fraction must be removed to produce a material suitable for beneficial use; this is typically a regulatory decision.

Physical testing of all samples should be conducted prior to any chemical fractionation testing, since the physical tests are fast and inexpensive, will yield data which may rule out separation as a viable approach, and will indicate which samples should undergo chemical analysis. Chemical fractionation testing should only be conducted if the physical data indicate

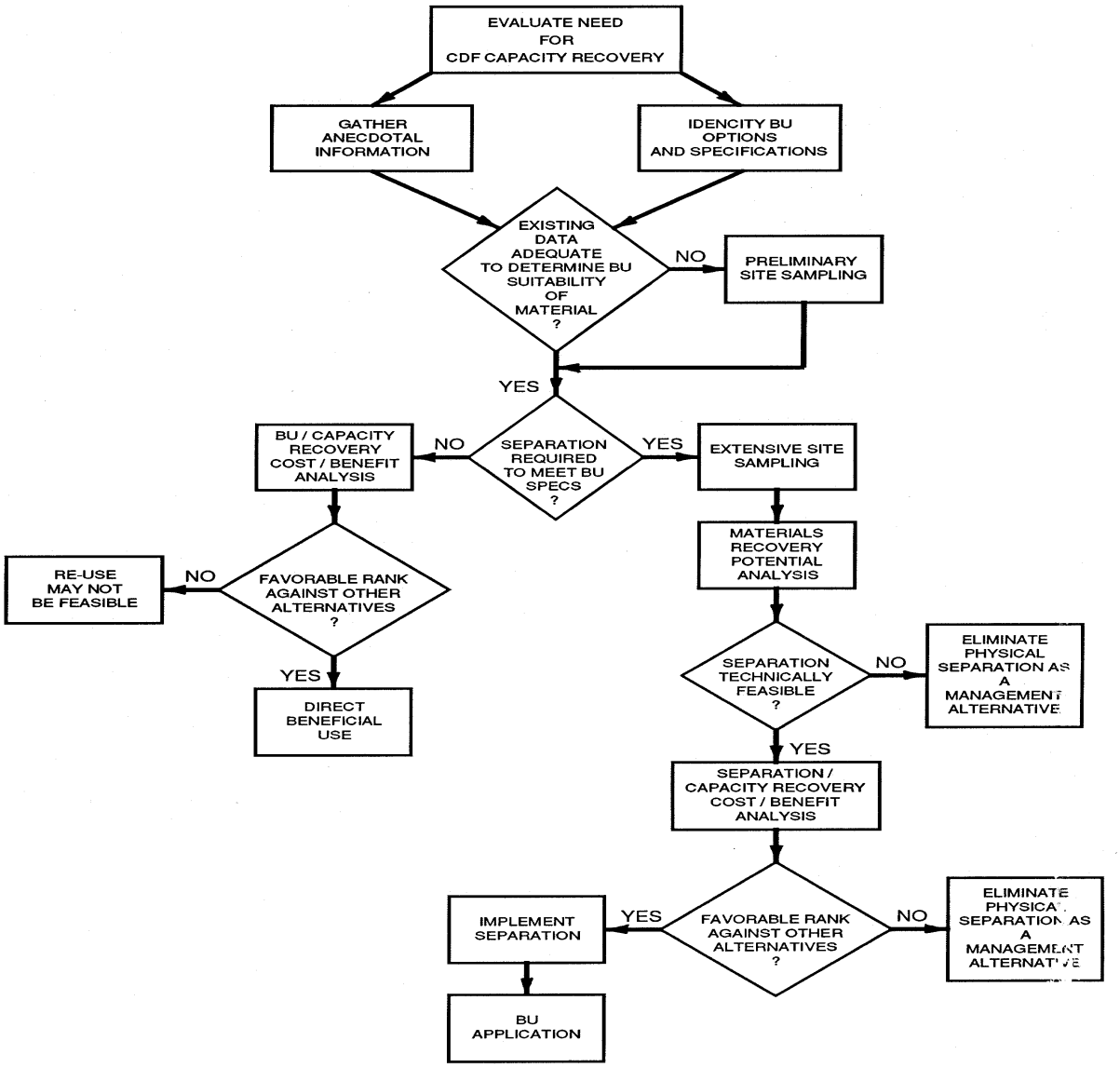


FIGURE 2-1. Evaluation of feasibility for BU recovery of dredged material.

feasibility. The physical data may also lead to strategies for compositing samples for the contaminant distribution (fractionation) testing.

Selection of analytes for chemical analysis is a key component of the feasibility evaluation, and will significantly impact the overall cost of the site characterization. Ultimately, this is a regulatory issue. For the purposes of preliminary site characterization, some cost savings can be achieved by limiting the number of analytes where possible. This may be done by doing a full suite of metals and organic compounds on a few bulk samples likely to represent the worst case contamination. Compounds which are not detected in the bulk analysis can be eliminated from most of the fractionation testing, although a full suite should be done on all fractions of some samples. A 250 ml (8 oz) sample of dry or high solids sediment is sufficient to conduct the following analysis, including standard QA/QC: Michigan Metals (Arsenic,

Barium, Cadmium, Chromium, Copper, Iron, Lead, Mercury, Nickel, Selenium, Silver, and Zinc), and organic compound groups including base neutral/acid extractable (semivolatiles, BNA), polyaromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), and total recoverable petroleum hydrocarbons (TRPH). Additional material is required initially to produce this volume in each resulting fraction. Necessary starting sample volumes can be estimated from the bulk grain size distribution. If the volume of any fraction obtained following separation is insufficient, fractions may have to be composited, or limited analysis conducted, to obtain as much information as possible from those samples. Multiple samples may be composited only if this is representative of the manner in which the material will be blended for processing.

Existing characterization methods include the Fingerprint method and the TDG method. The Fingerprint method was developed by Heidemij Realisatie, now ARCADIS Realisatie (Olin et al. 1999), and is a pilot scale operation using hydrocyclones to produce six size fractions, followed by gravity separation of the density fractions. The TDG method is a bench scale characterization procedure developed by ARCADIS Realisatie and TNO Institute of Environmental and Energy Technology (Olin et al. 1999), producing three size fractions and three density subfractions. Test development for contaminant distribution determinations is an on-going research effort under the DOER program. Efforts are being directed to streamline and standardize the process and minimize costs, employing mineralogically significant size cutpoints (silt/sand and clay/silt) and an innovative density separation process. The procedures under development utilize equipment that is widely available (Olin et al. 1999). Contaminant distribution studies examining relative contaminant distribution behavior and the contribution of the clay fraction to overall contaminant levels are being conducted in connection with this effort. Guidance on this work will be provided in a subsequent publication.

PHYSICAL SEPARATION PROCESSES

The information contained in this section was summarized from Olin et al. (1999) to which the reader is referred for a more in-depth discussion of physical separation processes and equipment. "Much of the philosophy of volume reduction comes from hundreds of years of mining experience worldwide…The remediation engineer has the same challenge; to remove small amounts of contaminants from complicated and diverse feeds. Volume reduction uses a fundamental understanding of the physical and chemical characteristics of the feed soil or sediment and a simple, inexpensive treatment train to remove clean material. This results in a smaller mass of contaminated material to be either further treated or disposed." (Olin et al. 1999). The focus here is on physical separation, but physical separation processes can be, and often are, coupled with chemical treatment and extraction processes. The principal properties utilized in separation of sediment fractions are particle size and density. Surface chemistry and magnetic properties may play a role in isolated cases, but the vast majority of separations are made on the basis of size and density. Additionally, with the exception of screening processes, most separations are not purely size or density separations. While one parameter may predominate, some density effects will be felt in a size separator, and vice versa. There are five principal components of physical separation treatment trains: pre-screening, primary physical size separation, density separation, solid/liquid separation and dewatering (Olin et al. 1999).

"Pre-screening refers to the removal, or reduction in size, of oversize materials from the bulk sediment that would interfere with downstream processing operations. Oversize materials

are roughly 50 mm in size or larger." (Olin et al. 1999). Dredged material oversize may consist of stones, tree limbs, and soil clumps, but may also include such unwieldy objects as cable, refrigerators, tires or car bodies. As a result, the pre-screening component may present some difficult challenges for dredged material processing operations. "Prescreening equipment may involve one or more of the following: feed hoppers, fixed bar screens (grizzlies), rotating trommel screens, comminutors, attritioners, log washers and hand picking" (Olin et al. 1999).

Size separation is the central unit operation of the physical separation treatment train. "Because many contaminants associate chiefly with the finer soil fractions, separation of sand size particles (>75 μm) from silts and clays (<75 μm) is typically the foundation on which the remainder of the soil washing treatment train is established and refined. Size separation equipment may include one or more of the following processes: screens (fixed or vibrating, wet or dry), hydrocyclones and sieve bends" (Olin et al. 1999).

Density separation is useful when there are significant amounts of either low density organic material, or high density metal fragments. Most mineral components of sediments do not differ enough for density separations to be valuable, but sediments and dredged material may well contain various amounts of organic material that can be successfully separated from the mineral fraction. Because anthropogenic contaminants have a high affinity for organic material, removal of organic material may be necessary to produce a clean fraction, even within the coarsest materials. "A density separation circuit might include: spiral concentrators, mineral jigs, multi-gravity separators, dense media, shaking tables or a pinched sluice. Spiral concentrators and jigs are most commonly utilized in remediation" (Olin et al. 1999).

With the possible exception of prescreening for oversize material, physical separation processes require that the material be slurried with water for processing. The high volume of water introduced is one of the chief disadvantages of physical separation as a management strategy. "Gross separation of the solids and water is achieved with solid/liquid separation processes, typically utilizing clarifiers, sedimentation basins, lamella clarifiers or flotation cells" (Olin et al. 1999).

Dewatering is essentially a second stage solid/liquid separation process, necessary to produce a material dry enough to handle. "Solids concentrations of 45 percent to 80 percent are possible, depending upon the size of the material and the dewatering processes used. Fine materials are the most difficult to dewater and typically represent a significant portion of overall processing costs. A dewatering circuit might utilize one or more of the following: screens, belt filter presses, plate and frame filter presses, centrifuges, screw classifiers or rotary vacuum filters" (Olin et al. 1999).

More detailed descriptions of the above referenced equipment are available in Olin et al. (1999), and include feed requirements, capacity and, where available, general capital and operating cost ranges. Sample treatment trains and case studies are also described in Olin et al. (1999).

DETERMINATION OF MRP

Data Requirements. Several types of data are required to estimate MRP:

1. Bulk sediment data: Volume of available bulk sediment or dredged material, grain size distribution (GSD) of the bulk material (prior to separation), concentration of contaminants of concern (COC) in the bulk sediments

2. Beneficial use specifications, including acceptable grain size distribution, COC levels, and quantity, seasonal and logistical requirements
3. Concentrations of COC in material fractions, if separation is determined to be necessary to meet beneficial use specifications.

Information Sources. Project surveys and data from prior testing are the most likely sources of existing information. Although materials to be dredged or previously disposed in a CDF are typically characterized to some degree, both physically and chemically, this information was likely not obtained or structured with an eye toward evaluation of material recovery potential and separation feasibility. Even so, percent sand and bulk contaminant levels are usually known, and can be useful for initial screening and MRP estimates, if the coarse material is assumed to be relatively clean. More targeted sampling and analysis will likely be required to obtain definitive information.

While project data related to sediment physical and chemical characteristics as described above is usually available for a number of stations in the case of in-channel evaluations, spatial data is rarely available for in-CDF materials. Some idea of material properties in the CDF must be inferred from existing in-channel data, CDF site surveys and visual inspections of the CDF surface, and knowledge of CDF filling operations. In both in-channel and in-CDF locations, additional data should be obtained through sampling and testing if the initial screening evaluations indicate separation may be necessary and feasible. Olin-Estes and Palermo (2000) and Olin-Estes (2000) contain further guidance on prescriptive and statistical sampling approaches, respectively.

Volume Estimates. The volumes of material available, either in-channel or in-CDF, will be defined by survey information. Volumes available, either on a periodic basis or on a one-time basis, must be comparable to those required for the BU application and must be large enough to achieve economies of scale. Also, the effect of bulking and of concentration of COCs in the separated fine fraction must be evaluated in determining CDF capacity ultimately recoverable.

Material Specifications. The principal material specifications are typically related to grain size and contaminant level. The specifications for acceptable grain size for a given BU application will depend on the intended application. From the physical standpoint, the material specifications may be an average grain size (D_{50}) or a target grain size distribution. The specifications may also include an acceptable percentage of material finer or coarser than the desired range. For example, Figure 2-2 illustrates the desired grain size range for a BU application for beach nourishment (note that specifications will be site specific).

Acceptable levels of COC are usually a function of environmental regulations or guidelines pertaining to the type of activity associated with the BU application. Normally, these criteria or standards will include specific concentrations of contaminants allowable, on a dry weight basis, in a material intended for a specific BU. Regulatory agencies in some states have proposed or adopted policies which encourage re-use of materials and provide for a case by case review and determination of requirements (Olin 1998).

As previously discussed under material characterization, the material specifications for anticipated beneficial uses should first be compared to the bulk material properties (as they exist prior to any separation) to determine if the material can be used beneficially as is. Because chemical analysis is extremely expensive, physical parameters, which can be quickly and

inexpensively determined, should be evaluated first. Grain size distribution may rule out certain beneficial uses without any further analysis, or help to target a limited number of samples for chemical analysis if the grain size distribution is compatible with the proposed beneficial use. Depending upon the variability of the site, the grain size distribution may be an average for the whole site, or a section or sections of the site under consideration. If the grain size distribution is acceptable, it should then be determined if the COC in the bulk material are at levels below all limiting concentrations for the BU application. If all COC are at concentrations below the BU requirements and the material GSD falls within the BU specifications for the entire site or portion under consideration, no separation is needed and the material can be applied to the BU as is. This is illustrated Figure 2-3. The MRP evaluation in this case is simply to determine if the volumes available on a one-time or recurring basis will meet the needs for the BU application under consideration.

If the bulk material does not meet requirements as is, the potential for separation to meet the requirements must first be assessed in general terms. A number of factors should be considered: preliminary targeted size or density cut, the technical difficulty of making the targeted separation, potential for regulatory classification changes in concentrated residual materials. The simplest separation from a technical perspective is a sand/silt separation. A silt/clay separation is technically more difficult, but may be worth considering if removal of the clay would permit recovery and reuse of the silt fraction as well. Acceptable COC levels in residual materials would be tied to any threshold which may require an increased level of treatment or management as compared to the pre-separation condition, e.g., the 50 ppm threshold for PCB triggering management under the Toxic Substances Control Act (TSCA). Cost to manage such materials must be considered in the economic analysis if the potential to produce them exists. Preliminary chemical characterization will be important in this regard.

Screening criteria can be applied for the entire sediment mass within a waterway or to specific reaches within the waterway if such reaches define areas with similar characteristics, or if the reaches will be separately handled. Similarly, the screening criteria can be applied to the entire dredged material mass within the CDF for proposed reclamation or to separate zones, such as areas with materials having higher coarse fractions (such as mounds near inflow points). Compositing of samples during characterization should be done carefully, however. If separation is planned, samples should not be composited unless materials will be blended in a similar manner for processing (Olin et al. 1999).

Calculation of MRP. The calculation of MRP is derived from a comparison of the grain size distribution of the material to the BU specification (assuming COC levels are acceptable) and an estimate of the tons dry weight of material available. Assuming that the available grain size distribution and contaminant data point to separation as a possible management approach, the MRP following separation must be determined.

The definition of MRP is expressed in terms of tons dry weight of product for two reasons. First, volumes and wet weights may change with the relative gain or loss of water during separation or dewatering processes, but the dry weight of product is essentially constant. Second, project requirements for a product derived from separation would usually be expressed on a dry weight basis. This is especially true for products such as fine aggregates or manufactured soil products. Following separation, the product intended for BU and the residual material will have differing grain size distributions as compared to the bulk material distribution prior to separation.

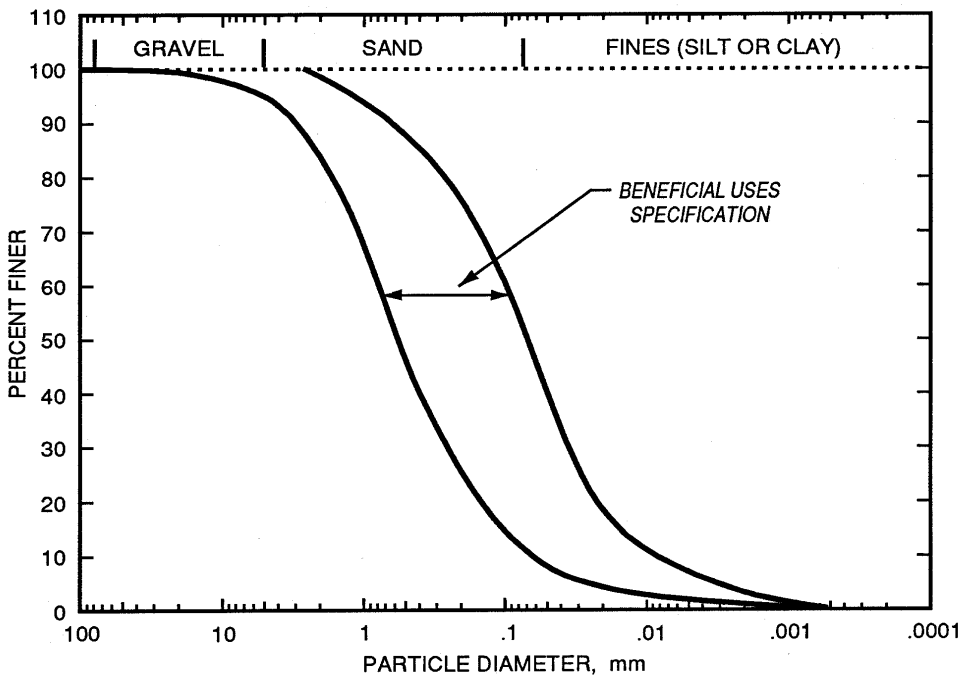


FIGURE 2-2. BU grain size specification example.

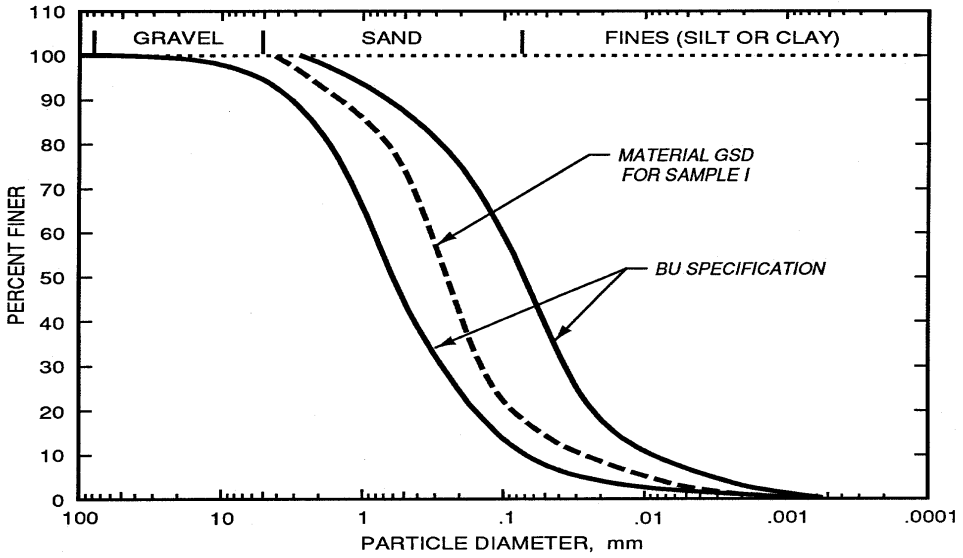


FIGURE 2-3. GSD falling within BU specification.

Figure 2-4 illustrates the typical case in which the desired product is specified as having a coarser grain size distribution than the initial material prior to separation. The specifications for an acceptable product will usually include a range of grain sizes, and this is illustrated by the band of distributions as shown in the figure.

The recommended method for calculating MRP is as follows:

$$MRP = \sum_{i=o}^{i=n} P_{si} W_{si} \qquad (2\text{-}1)$$

where

MRP = material recovery potential, tons
P_{si} = percentage by weight of sample grain size meeting the BU material specification for sample *i* (as a decimal).
W_{si} = dry weight of material represented by sample *i*, tons
n = number of samples considered.

The percentage of material in a given sample meeting the specifications, P_{si}, can be estimated based on the overlap of the GSD curve for that sample and of the BU specification range. Figure 2-4a illustrates a relatively small proportion meeting specifications, while Figure 2-4b illustrates a relatively large proportion of the material volume potentially meeting the specifications. The proportion meeting specifications (in percent) will determine the MRP. In cases where the BU specification is given as a single D_{50} grain size, the value of P_{si} can be determined as shown in Figures 2-5 and 2-6. Analytically, this can be expressed as:

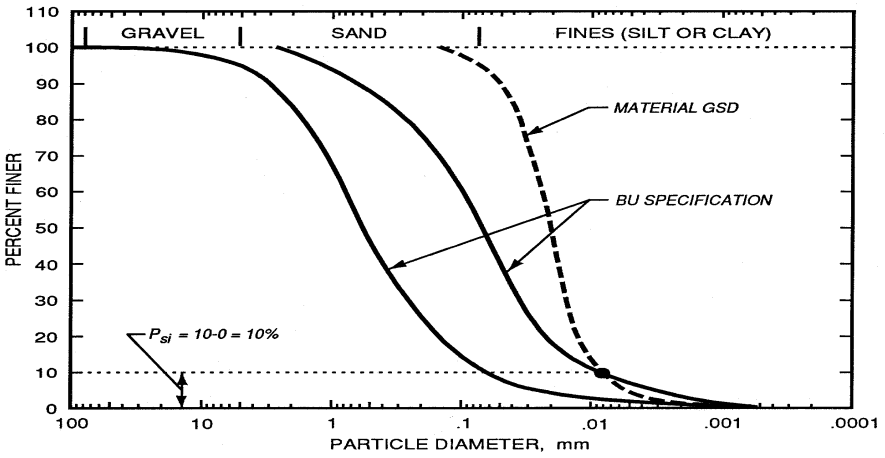
For $D_{50<}D_{50spec}$: P_{si} = (100 - percent passing D_{50spec}) x 2 (2-2)
For $D_{50>}D_{50spec}$: P_{si} = percent passing D_{50spec} x 2 (2-3)

The tons dry weight represented by a sample, W_{si}, can be estimated as follows:

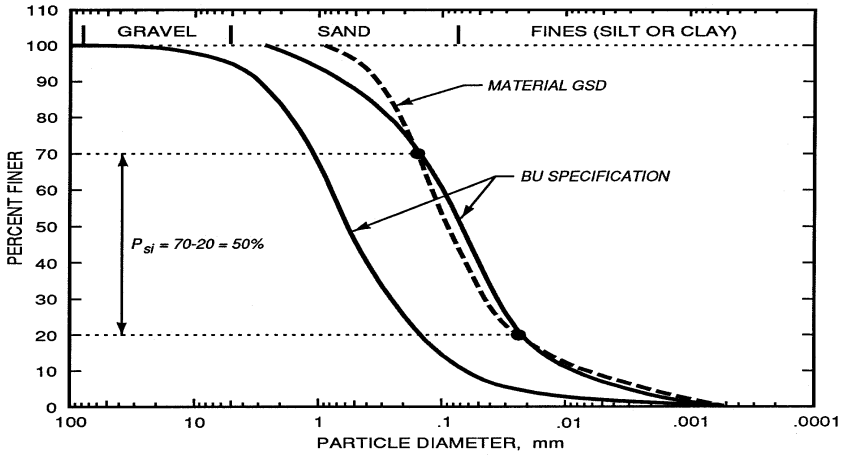
$$W_{si} = (0.0135)V_i(\gamma_i) \qquad (2\text{-}4)$$

where

W_{si} = dry weight of solids represented by sample i, tons
V_i = volume represented by sample i, cubic yards, (determined by survey data)
γ_i = unit weight of the dry material for sample i, lbs/cu ft
(determined based on water content or dry density measurement)
0.0135 = conversion factor



a. P_{si} = 10 percent



b. P_{si} = 50 percent

FIGURE 2-4. Recoverable percentage (P_{si}) for material having finer GSD than BU specification.

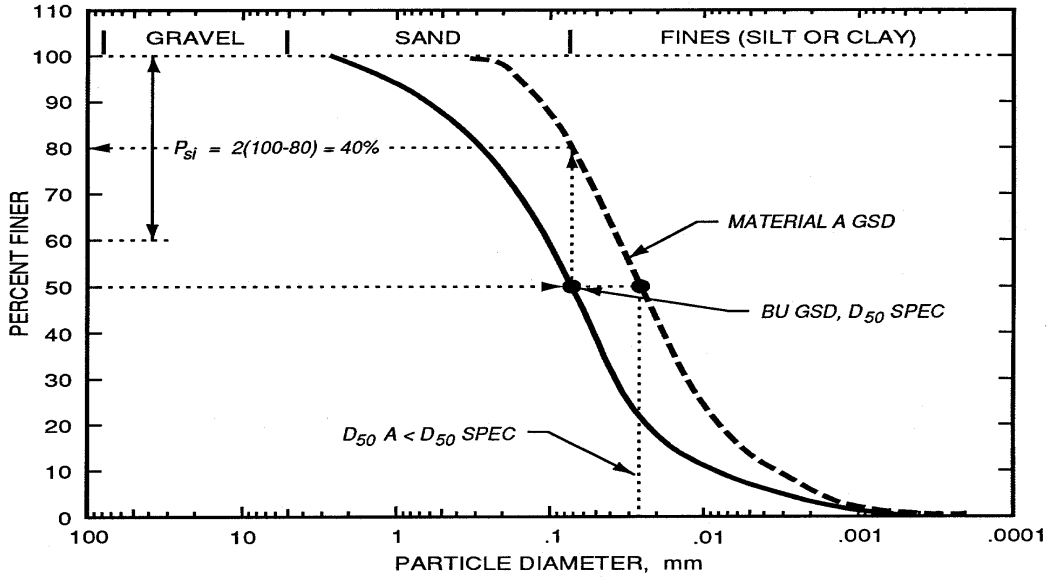


FIGURE 2-5. P_{si} for material with D_{50} < D_{50} BU specification.

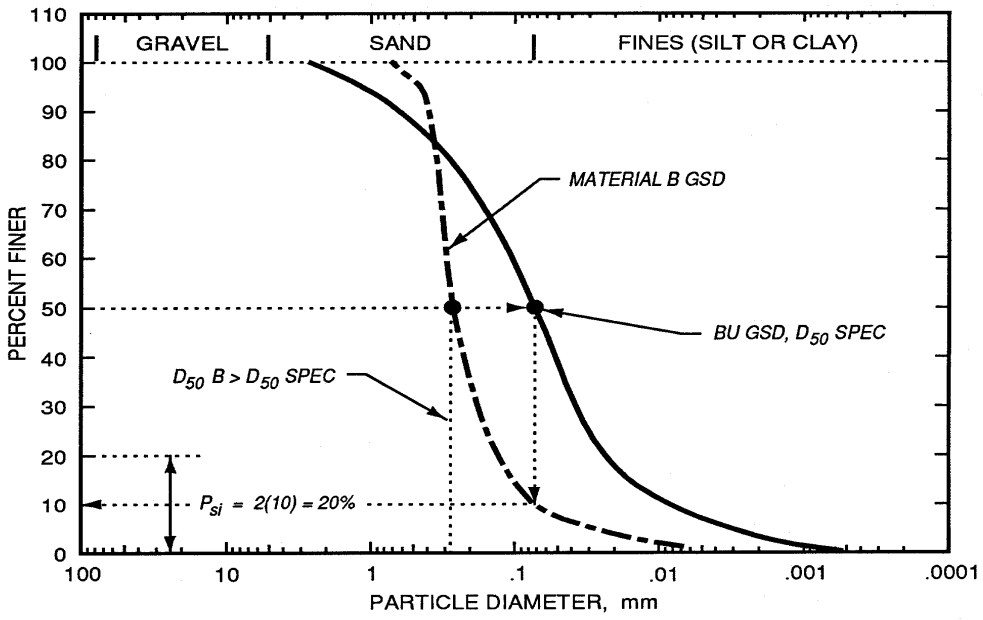


FIGURE 2-6. P_{si} for material with D_{50} > D_{50} BU specification.

The calculation method shown here can be applied in the same way for an initial evaluation using existing grain size distribution data or following collection of additional samples. The above relationship for calculating MRP can be applied to individual samples representing an incremental volume of the total, or an average of several samples representing either a composited volume, or the total volume of interest. This will be determined, as previously mentioned, based on the variability of the site and the expected compositing of the material for processing. Some data estimating approaches described in Olin-Estes (2000) may also be helpful in segmenting the volume between data points.

CONSIDERATION OF RESIDUAL VOLUME CHANGES

Although a proportion of the total mass dry weight of the material may be recoverable, the resulting increase in volume (bulking) of the residual materials should be evaluated in determining the advisability of separation. For example, if 50 percent by weight of the material in an existing CDF is removed, the resulting capacity recovered within the CDF will be less if hydraulic methods are used in the separation process. The residual fine fraction will increase in volume (bulking), at least in the short term. The same would hold true if hydraulic separation methods were applied as a follow on to mechanical dredging/rehandling operations. Residuals can be dewatered successfully, eliminating the problems resulting from bulking, but mechanical dewatering is typically one of the more expensive unit processes in a physical separation treatment train.

Methods for estimating the volumes occupied by hydraulically dredged material as a function of time and operational factors are given in Engineer Manual 1110-2-5027 (Headquarters U.S. Army Corps of Engineers 1987). These methods rely on column settling tests to evaluate volume changes during hydraulic placement of fine grained material, and may be applied directly in evaluating potential changes in volumes of fine grained fractions resulting from hydraulic separation methods. The calculations would require laboratory test data as described in EM 1110-2-5027, particularly as the overflow from a separation process will typically present a more dilute slurry than a hydraulic dredge discharge, for which this guidance was designed.

COMPLETION OF SEPARATION FEASIBILITY EVALUATION

Once a reliable estimate of material recovery potential has been developed, the information can be used in completing the evaluation of separation feasibility. If recovery potential matches the requirements for the BU applications under consideration, fractionation testing should be conducted to determine if separated fractions meet the requirements related to residual COC. If these results are favorable, appropriate operational methods or equipment for separation can be selected, and a cost analysis can be performed. Procedures for these aspects of the evaluation are described in Olin et al. (1999).

CONCLUSIONS

Development of a re-use plan for a CDF or dredging project will require a multi-step approach incorporating existing data, identification of local beneficial use opportunities and requirements, and practical and/or statistical sampling approaches. Physical separation is only

one of several approaches that can be taken to produce material suitable for various beneficial uses, and should be evaluated together with other alternatives to determine the most suitable approach for a given site.

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CHAPTER 3

DETERMINING RECOVERY POTENTIAL OF DREDGED MATERIAL FOR BENEFICIAL USE – SITE CHARACTERIZATION: PRESCRIPTIVE APPROACH[1]

BACKGROUND

The principal motivation for beneficial use recovery of dredged material is the growing shortage of storage capacity in confined disposal facilities (CDFs). The fundamental purpose of these tech notes is to assist in determining when material recovery is technically and economically feasible, and provide a strategy for obtaining and utilizing physical and chemical information necessary for this evaluation at the least possible cost. Olin-Estes and Palermo (2000) describe more fully the options existing to increase capacity, the fundamental approach to evaluating material recovery potential, and physical separation concepts. This note and Olin-Estes (2000) address informational needs. The fundamental approach is to begin with available information and progress to targeted sampling and analysis as needed.

The feasibility of separation as a management approach is dependent on several factors: ability to identify distinct fractions within the material meeting BU criteria, ability to separate suitable fractions, and material recovery potential (MRP) as determined by available volumes of suitable material. This technical note introduces a prescriptive approach to data acquisition for feasibility evaluation and MRP estimation that is generally applicable, whether or not separation is required to meet BU specifications. Olin-Estes and Palermo (2000) and Olin-Estes (2000) introduce physical separation concepts and more rigorous statistical sampling and data estimation methods, respectively.

INTRODUCTION

If available information is inadequate to determine compatibility of material for identified local beneficial uses (Olin-Estes and Palermo 2000), at least limited sampling of the material will be needed to make a preliminary determination. Preliminary sampling and data acquisition comprise the prescriptive site characterization described in this tech note. Figure 3-1 illustrates the place of prescriptive site characterization in the overall evaluation of feasibility for BU recovery.

DATA REQUIREMENTS

There are essentially two levels of MRP estimates: screening level, based on existing information, and definitive, based on more extensive site sampling. Several types of data are required to estimate MRP:

[1] Reproduced with permission from the U.S. Army Engineer Research and Development Center (ERDC), Vicksburg, Mississippi.

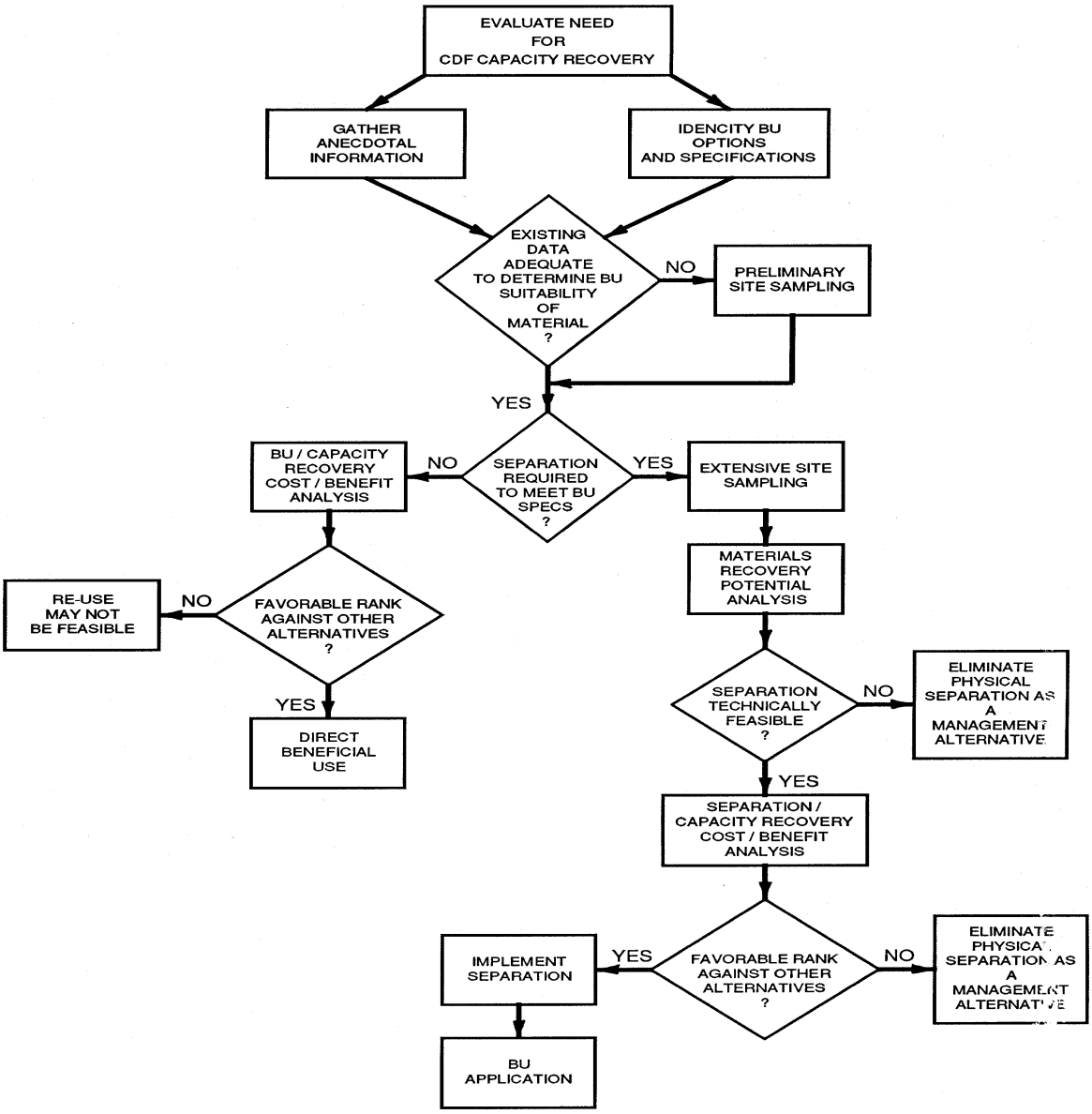

FIGURE 3-1. Evaluation of feasibility for BU recovery of dredged material.

- Bulk sediment data:
  - Volume of available bulk sediment or dredged material.
  - Grain size distribution (GSD) of the bulk material (prior to separation).
  - Concentrations of contaminants of concern (COC) in the bulk sediments
- Beneficial use specifications, including acceptable GSD and COC levels
- Concentrations of COC in material fractions, if separation is determined to be necessary to meet BU specifications.

Project surveys and data from prior testing are the most likely sources of existing information. Although materials to be dredged or previously disposed in a CDF are typically characterized to some degree, both physically and chemically, this information was likely not obtained or structured with an eye toward evaluation of material recovery potential and separation feasibility. Even so, percent sand and bulk contaminant levels are usually known, and can be useful for initial screening and MRP estimates, if the coarse material is assumed to be relatively clean. More targeted sampling and analysis will ultimately be required to obtain definitive information and to confirm this assumption.

While project data related to sediment physical and chemical characteristics as described above is usually available for a number of stations in the case of in-channel evaluations, data is rarely available for in-CDF materials. Some idea of material properties in the CDF must be inferred from existing in-channel data, CDF site surveys and visual inspections of the CDF surface, and knowledge of CDF filling operations. In both in-channel and in-CDF locations, additional data should be obtained through sampling and testing if the initial screening evaluations indicate separation may be necessary and feasible. Olin-Estes (2000) describes approaches for designing a more extensive sampling plan and interpreting data. Olin-Estes and Palermo (2000) more fully describe beneficial use specifications and COC considerations and provides mathematical relationships for using this information to calculate MRP.

In-channel Evaluations. Information particularly important for site characterization of projects prior to dredging (materials in-channel) includes:

- Shoaling rates and sediment volumes as a function of location and time within the waterway.
- Physical characteristics of the sediments in the waterway as a function of location and time, specifically the grain size distribution of the sediments in-situ.
- Contaminant distribution and magnitude for the sediments. Location of sources of contamination, such as industrial and sewage outfalls.

Hydrodynamics and the sources of sediments will govern the physical characteristics of the sediments in the waterway as a function of location and time. The target material from a waterway may be the total volume to be dredged for a given project or a portion of the total which can potentially meet the characteristics for BU, with or without separation. For example, past experience may indicate that sediments in certain reaches of a waterway or entrance channel tend to shoal with predominantly sandy sediments, while others shoal with fine-grained silts and clays. This information, when combined with volumes historically dredged from these reaches, give an indication of the relative volumes of sandy versus fine material likely to be generated by a dredging event. Grain size distribution data is normally available from past dredging evaluations. These data should be examined for every station sampled to determine which portions of the total shoal volume are potentially suited to BU, or may require separation to meet BU specifications.

In-CDF Initial Evaluations. The following information is particularly important for estimating reclamation potential of materials in an existing CDF:

- The area and likely thickness of material deposits in the CDF.
- Volumes, frequency and rates of placement for materials in the CDF.
- Physical characteristics of the sediments in the CDF as a function of location and depth, specifically the grain size distribution of the sediments in-situ.
- Chemical characteristics of the COC as related to known sediment physical characteristics.

Some of the above may be inferred with knowledge of inflow and outflow points, disposal methods, and site operation and management practices. Material hydraulically placed in a CDF tends to separate to some degree due to the sedimentation process occurring within the site. Field data has provided information on the general behavior of dredged material in CDFs with respect to this particle sorting or separation. Several CDFs in the Great Lakes were evaluated in the 1970s, each filled with predominantly fine-grained dredged material initially containing only a small fraction of sand. Grain size data indicated that all of coarser sandy material settled in the CDF within a distance of 100 m from the inflow point. The grain size properties of the finer material were generally consistent in the larger portion of the CDF, with some clay-size material settling near the outflow weirs (Krizek 1976).

In general, for hydraulically filled CDFs, coarse-grained material (sand size and above) will tend to accumulate at the point of inflow. In fact, for many projects, the inflow pipes must be moved often to avoid build-up of high mounds of sandy material. The finer silts and clay also tend to separate to some degree, with a mixture of silts and clays spread from the mounded coarse material near the inflow area to near the outflow weirs. In some cases, finer clay fractions may accumulate in higher proportions toward the outflow points. The degree to which this occurs depends on the geometry of the CDF, the locations of inflow points and outflow weir structures, and operational factors such as the depth of ponding and flowrate during a particular filling operation.

Material distribution within a CDF may be more variable for mechanically dredged sediments than for hydraulically dredged sediments, depending upon the offloading method. Material is offloaded by mechanical means at many CDFs in the Great Lakes area. The material is typically offloaded from one or more points around the CDF. Mechanically dredged and offloaded material does flow, but will not exhibit significant particle size separation from settling.

Valuable information for a screening level evaluation can be obtained from a site visit and visual survey of conditions within the CDF, and a field inspection should always be conducted at this stage of evaluation. More information can be obtained if the CDF is easily accessible and the surface has been exposed to drying. Surficial samples will likely be helpful in the preliminary evaluation stage to determine surface material distribution by grain size in the CDF. Some chemical analysis should also be done to obtain some indication of the types of contaminants present, and the contaminant levels of the bulk and separated material.

The operational history of the CDF and natural settling processes may be taken into account in developing a screening-level estimate of the MRP. It should be noted that any such estimate should take into account the three-dimensional aspect of the site. Figure 3-2 shows a CDF with multiple layers of material placed at intervals, each with its own mounded area of coarse strength prior to the next filling operation to support sand mounds. So, reliance on just a surficial delineation of the coarse-grained area may lead to errors in volume calculations. To avoid this, the relative percentages of coarse material in each filling event could be taken into

account. Ultimately, core samples must be taken to verify distribution of material and refine recoverable volume estimates.

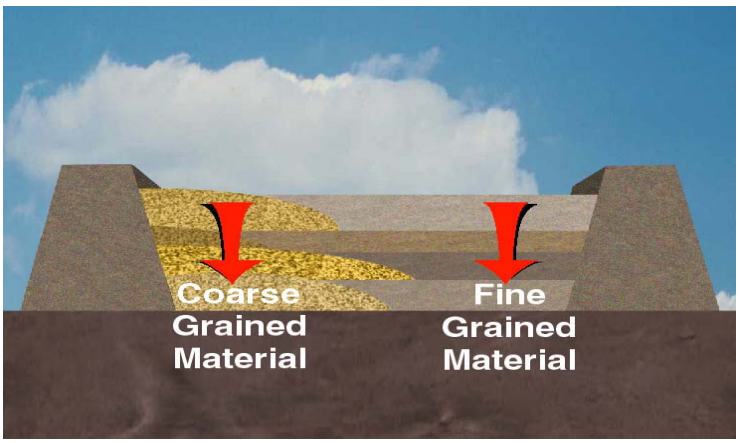

FIGURE 3-2. Typical layering of materials in hydraulically filled CDF.

Results of Initial Evaluation. If existing data and surficial sampling are sufficient to determine BU suitability of the material and separation requirements, no further sampling is required. However, in many cases, grain size distribution data available from tests run on in-channel materials, or surficial samples, will not be representative of the grain size distributions throughout the CDF. Additionally, fractionation testing to determine contaminant distribution is not generally done as a part of normal operating procedures. In most cases it is expected that a more detailed evaluation will be required to quantify and characterize the material. This will typically involve core sampling to the full depth of the deposit for CDFs. Two approaches can be taken for site sampling, depending on the scale and nature of the project, prescriptive, described in later sections of this technical note, or statistical, as described in Olin-Estes (2000).

GENERAL CONSIDERATIONS FOR ADDITIONAL SAMPLING

Guidance on site characterization for in-channel sediments is widely available (U.S. Environmental Protection Agency (USEPA)/ U.S. Army Corps of Engineers (USACE) 1998), while such guidance for sampling material placed within a CDF is limited at present. A touchstone of all guidance presently available is the need for a written sampling and testing plan. Such a plan should be developed, reviewed and approved by appropriate stakeholders prior to execution. Guidance on sampling plan development is available (USEPA/USACE 1998; Headquarters USACE 1994; Olin-Estes 2000).

The sampling strategy or plan must be developed to characterize either the entire site (in-channel or in-CDF) or portions of the site with potential for material recovery. The number and location of samples should be the minimum required to adequately characterize the materials and allow a reliable estimate of material recovery potential. Prescriptive evaluations rely on a limited number of samples applied to selected areas, based on the existing data and knowledge of

the behavior of the materials and management of the site. Statistical approaches determine sample numbers and locations based on the variability of material properties. In general, statistical approaches will require a higher number of samples than prescriptive approaches, but have the advantage of facilitating statistical analysis of data obtained and providing established methods to extrapolate data to unsampled areas.

It may be possible to coordinate a single sampling effort to meet a number of project needs; the design of the sampling program for material recovery potential should be closely coordinated with other sampling requirements to avoid duplication and reduce costs. Examples of other sampling and testing requirements which could conceivably be done concurrently with an evaluation of BU and separation feasibility may include that required to evaluate other sediment treatment approaches such as bioremediation, or manufactured soil.

Extensive guidance on sampling methods and equipment is available (Mudroch and McKnight 1993). The approaches would differ, however, for in-channel versus in-CDF sampling programs. The testing requirements will influence the type of sample and volume of sample as well as the sample handling and preservation requirements. For purposes of evaluating BU and separation feasibility, determination of material grain size, bulk sediment chemistry (with respect to COC), and associated fractionation of COCs with grain size or density ranges, are the normal objectives of testing. Sample volume requirements and analyte selection are further discussed in following sections.

PRESCRIPTIVE GUIDANCE ON SITE CHARACTERIZATION

The prescriptive approach to sampling and testing determines an appropriate number of samples and selection of sampling locations based on sound judgment, considering project conditions and regulatory requirements. Past testing and characterization data and anecdotal evidence such as knowledge of shoaling and sedimentation patterns in waterways, or prior experience with behavior of materials as placed in CDFs, serves as the basis of such an initial evaluation. The numbers of samples using the prescriptive approach would likely be much lower than those indicated by statistical approaches described in Olin-Estes (2000). Guidance on in-channel site characterization is widely available (USEPA/USACE 1998) and is applicable in the context of evaluating material recovery potential. Depending on the beneficial use options under consideration, a sampling effort for material recovery potential can be focused on specific areas within a waterway or within a CDF, to obtain the most information for the least effort and cost. Targeted sampling is only possible when information on the distribution of material properties within the overall site is available. However, there are considerations which should be emphasized for selection of the optimum sampling locations and numbers of samples.

Sampling Locations. Sample locations can be selected using a uniform (grid) approach or a clustered approach, with the clusters concentrated on areas of interest. If the initial evaluation of existing data provides some indication of areas within the waterway or CDF with higher potential for material recovery, a clustered approach will save resources and provide a better definition of material characteristics for those areas with higher recovery potential. Areas with low potential can be either not sampled or sampled with a very low resolution to confirm the existing data and historical record. Selection of sampling locations within CDFs should be guided by known behavior of materials hydraulically or mechanically placed in the CDF. The fact that coarser material tends to accumulate adjacent to the inflow points for hydraulically

placed sediments can be used to cluster locations toward specific areas within the site, assuming recovery of coarse materials is likely the objective.

Spacing. The spacing between stations will be governed by the variability of the material within the site, the overall size of the areas to be sampled, and total number of stations deemed affordable, considering the scale of the project and funding constraints.

Depth of Sampling. The depth to which material in-channel should be characterized should extend to the full depth of anticipated dredging. Multiple samples at depth at a given location would not be required to provide vertical resolution if the dredging depth is only a few feet (say <3ft (0.9 m)) and the material appears to be relatively homogeneous throughout this depth. For maintenance projects, previous data may indicate if vertical differences in sediment composition are evident even with greater shoal thickness. For new work, or for cases where maintenance dredging has not taken place in many years, some sampling at depth will be required to define vertical resolution.

Depth of sampling within a CDF is dependent on the lift thickness, as estimated using the area of the CDF and the volumes placed in each specific filling operation. As shown in Figure 3- 2, the three-dimensional layering pattern formed by natural separation of coarse and fine material may influence the depths at which samples are taken, and the depth of sampling could be different for different areas within the CDF. Sampling at depth within a CDF will normally be accomplished with core samples.

Sample Replication and Sample Compositing. Other than standard QA/QC (USEPA/USACE 1995) sample replication is generally not a regulatory requirement for characterization data, either physical or chemical. However, taking multiple samples for analysis from a homogenized sample increases the reliability of the data. This concept is further described in following section (Sample Size Required). Samples taken from different locations on the site are not generally composited, unless the material will be blended for processing. Even in this eventuality, it may be more valuable initially to analyze samples individually to better define overall site variability. Sections of sample cores, however, will be composited and a small sample taken from some or all of these intervals for chemical analysis. Determination of appropriate compositing intervals is an important element of the testing strategy. Pre-screening based on visual inspection of grain size, color and odor may facilitate this determination. Once individual characterization samples are tested, the results can then be used to select a scheme for compositing samples for further testing as a cost savings measure. In addition, some statistical sampling approaches utilize sample compositing, as is described in Olin-Estes (2000).

Sample Size Required. Sample size refers to the volume of material that is homogenized and then sampled for analysis. For example, if a 1.8-(6-ft) core is taken, it will normally be subdivided into smaller sections which are thoroughly homogenized and then a very small subsample of each homogenized section is taken for chemical analysis. Because sediments and the distribution of contaminants within the sediments are typically very heterogeneous, homogenization volume is a relatively important factor in obtaining data that are representative of site conditions. The greater the volume being homogenized, the more difficult the task to mix the sample adequately to produce a truly uniform sample. However, the more heterogeneous a material is, the larger the homogenization volume required to capture randomly distributed

components. Figures 3-3 and 3-4, adapted from Bourbie, Coussy and Zinzsner (1987), illustrate this concept for the measurement of acoustic properties of porous media; the chief difference being that measurement of macroscopic mechanical properties takes advantage of the entire homogenization volume, while measurement of contaminant concentrations or physico/chemical properties utilizes only a very small fraction of the selected homogenization volume. Figure 3-3 is a conceptual drawing of a porous media with the solid particles (gray), pore spaces (white) and inclusions of some type (black). By analogy, one can picture the inclusions as contaminated sediment particles mixed in with clean particles, and the effect of increasing volume in capturing a representative number of these inclusions in each homogenization volume. A volume that is too small may not capture any inclusions. One that is too large will capture many inclusions, but will be difficult to homogenize to uniformity; the results may be more reflective of the averaging that occurs with material blending, and fail to provide information regarding the overall range of variation of the component of interest. Again, the fact that only a small fraction of the homogenized volume is actually utilized for chemical analysis emphasizes the value of taking multiple samples from each homogenization volume in defining variability. As indicated in Figure 3-4, some properties of porous media approach an asymptotic value at a given volume. This concept should be applicable to estimation of properties that can be measured using most or all of the homogenized sample, but the application to contaminant analysis is dubious because only a small fraction of the sample is analyzed.

Physical Testing. Physical testing of all samples should be conducted prior to any chemical fractionation testing, since the physical tests are fast and inexpensive and will yield data which may rule out separation as a necessary or viable approach, and indicate which samples should undergo chemical analysis. Chemical fractionation testing should only be conducted when separation appears to be necessary to meet BU requirements, physical data suggest that BU specs could be met with separation, and separation appears to be technically feasible. The physical data may also lead to strategies for compositing samples for the contaminant distribution (fractionation) testing. Several testing methods are described in Olin-Estes and Palermo (2000).

Chemical Analysis. Selection of analytes for chemical analysis is a key component of the feasibility evaluation, and will significantly impact the overall cost of the site characterization. Ultimately, this is a regulatory issue. For the purposes of preliminary site characterization, some cost savings can be achieved by limiting the number of analytes where possible. This may be done by doing a full suite of metals and organic compounds on a few bulk samples likely to represent the worst case contamination. Compounds not detected in the bulk analysis can be eliminated from most of the fractionation testing, although a full suite should be done on all fractions of some samples as confirmation. Sample volume required to conduct a full suite analysis on each fraction is discussed in more detail in Olin-Estes and Palermo (2000).

COMPLETION OF BU AND SEPARATION FEASIBILITY EVALUATION

Once a reliable estimate of material recovery potential has been developed using the procedure outlined in TN C13, the information can be used in completing the evaluation of BU/separation feasibility. If recovery potential matches the requirements for the BU applications under consideration, and separation is required, selection of appropriate operational

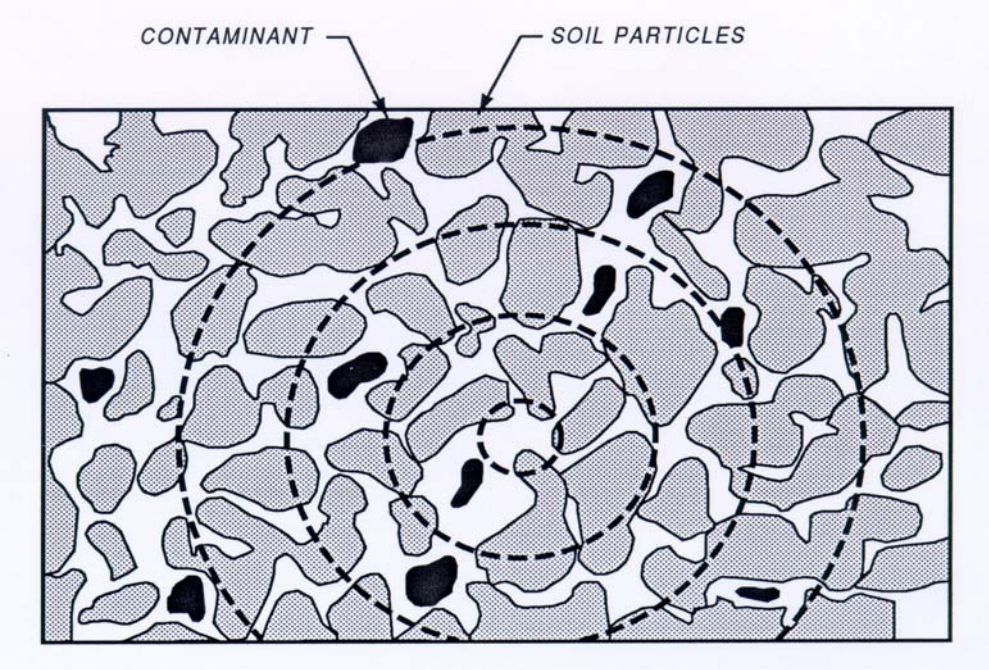

FIGURE 3-3. Effect of increasing sample size in capturing scattered soil inclusions (adapted from Bourbie, Coussy and Zinszner 1987).

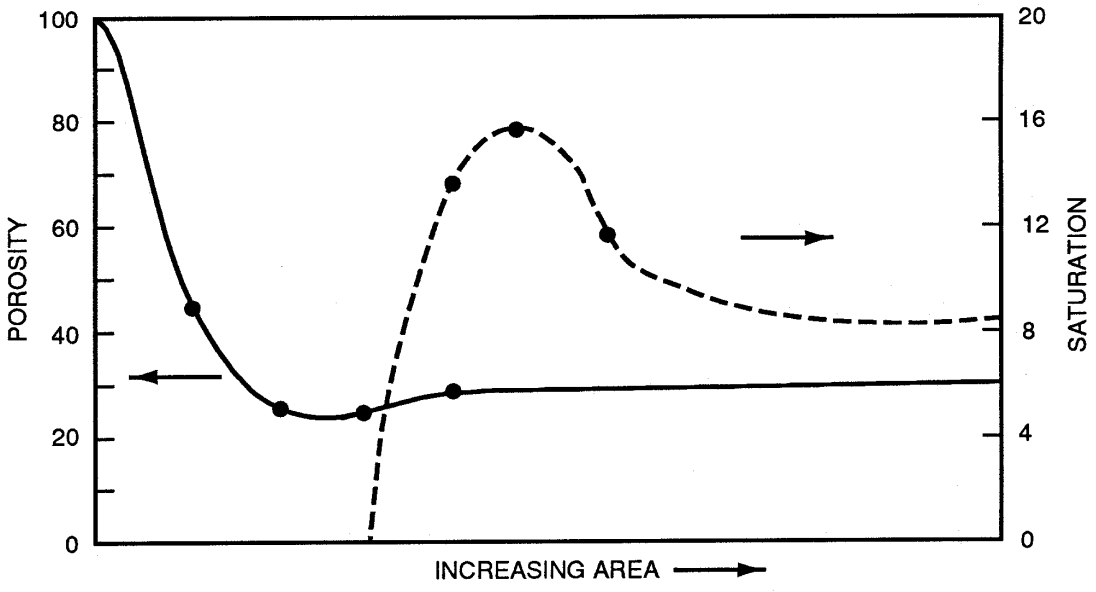

FIGURE 3-4. Asymptotic behaviour of porous media characteristics with increasing sample size (adapted from Bourbie, Coussy, and Zinszner 1987).

methods or equipment for separation and a cost analysis can be performed and the final decision on separation feasibility made. Procedures for equipment selection and cost estimating are described in Olin et al. (1999).

CONCLUSIONS

Development of a re-use plan for a CDF or dredging project will require a multi-step approach incorporating existing data, practical and/or statistical sampling approaches, and identification of local beneficial use opportunities and requirements. Little field verification is presently available regarding the efficacy of one sampling approach over another in characterizing the distribution of materials in a CDF. As further field experience is gained, refinements can likely be made that will result in an optimal approach and greater confidence in the results. Physical separation is only one of several approaches that can be taken to produce material suitable for various beneficial uses, and should be evaluated together with other alternatives to determine the most suitable approach for a given site.

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CHAPTER 4

DETERMINING RECOVERY POTENTIAL OF DREDGED MATERIAL FOR BENEFICIAL USE – SITE CHARACTERIZATION: STATISTICAL APPROACH[1]

BACKGROUND

The principal motivation for beneficial use recovery of dredged material is the growing shortage of storage capacity in confined disposal facilities (CDFs). The fundamental purpose of these tech notes is to assist in determining when material recovery is technically and economically feasible, and provide a strategy for obtaining and utilizing physical and chemical information necessary for this evaluation at the least possible cost. The fundamental approach is to begin with available information and progress to targeted sampling and analysis as needed.

Olin-Estes and Palermo (2000a, 2000b) introduce physical separation concepts and methods for estimating MRP, and prescriptive (limited sampling) site characterization methods, respectively. The feasibility of separation as a management approach is dependent on several factors, including ability to identify distinct fractions within the material meeting BU criteria, ability to separate suitable fractions, and MRP as determined by available volumes of suitable material. This chapter introduces statistical sampling and data estimation methods for extensive site characterization.

INTRODUCTION

When separation appears to be necessary to meet material specifications for identified beneficial uses, more detailed sediment/site characterization and evaluation is needed to estimate MRP. Extensive site sampling and data interpretation is addressed in the following sections. Figure 4-1 illustrates the position of extensive site sampling and characterization in evaluating feasibility of BU recovery. Olin-Estes and Palermo (2000b) describe the overall evaluation approach more extensively.

DATA REQUIREMENTS

The objective of extensive site characterization is to address the same data requirements as described in the two previous technical notes. These requirements are repeated here for clarity and ease of reference. There are essentially two levels of MRP estimates: screening level, based on existing information, and definitive, based on more extensive site sampling. Several types of data are required to estimate MRP:

- Bulk sediment data:
  - Volume of available bulk sediment or dredged material.

[1] Reproduced with permission from U.S. Army Engineer Research and Development Center (ERDC), Vicksburg, Mississippi

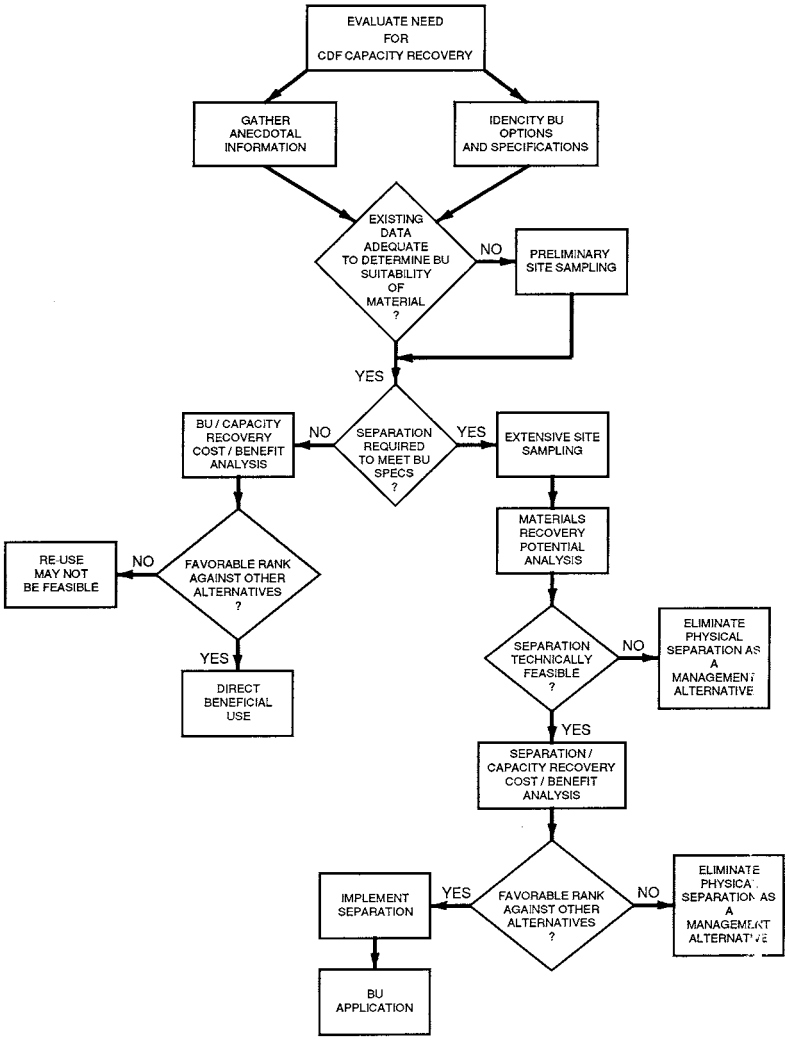

FIGURE 4-1. Evaluation of feasibility for BU recovery of dredged material.

  - Grain size distribution (GSD) of the bulk material (prior to separation).
  - Concentrations of contaminants of concern (COC) in the bulk sediments.
- Beneficial use specifications, including acceptable GSD and COC levels.
- Concentrations of COC in material fractions, if separation is determined to be necessary to meet BU specifications.

Use of existing information to obtain screening level estimates of MRP is described in Olin-Estes and Palermo (2000b). This chapter addresses the case in which existing information is inadequate for definitive determination of BU feasibility and MRP. Because data is rarely available for in-CDF materials, and because physical and chemical data for in-channel materials is not generally obtained specifically for determination of BU potential or physical separation feasibility, most projects of any size will ultimately require an extensive sampling effort.

General sampling considerations (sampling methods and equipment, sample volume requirements, analyte selection, depth of sampling, sample replication and compositing and

physical testing) are the same for both the statistical and prescriptive site characterization approaches. These are discussed fully in Olin-Estes and Palermo (2000a). This chapter addresses specifically the statistical basis and procedures to developing a site sampling plan and interpreting and extrapolating data.

SITE CHARACTERIZATIONS USING STATISTICAL APPROACHES

In designing a sampling plan, in addition to utilizing available information about the site, it is often helpful to look at the tools available for interpretation of the resulting data. There are a number of statistically based approaches which provide tools for determining the number of samples required to determine a measured parameter with a specified degree of confidence, unbiased approaches for structuring a sampling plan, and methods for interpreting and extrapolating data (Winkels and Stein 1997; Keillor 1995; Keillor 1993; Lubin, Williams and Lin 1995; Isaaks and Srivastava 1989). Given the constraints of time and budget, the number of samples required based on statistical considerations will often be much larger than is physically or economically feasible to obtain or analyze, unless the variability of the material is quite low. However, a sampling plan certainly should not be implemented without considering a statistical design, even though modifications to that design may ultimately be required. The resulting data will then lend itself to statistical analysis and available methods for extending the data to unsampled areas.

Statistical Analysis. In general, the larger a data set is, the more it tends toward a normal distribution. This is important because when we can establish that data is normally distributed, there are a number of statistical tools at our disposal to help us interpret the significance of differences between samples, and to predict the likelihood of values falling outside a specified range. Among these are the T-Test, the Paired Difference Test and Analysis of Variance (ANOVA). However, most environmental data is not normally distributed. Due to cost constraints, the data sets are too small, or may contain many zero values due to the heterogeneity of deposits and the difficulty of obtaining representative samples. Because environmental data does not always meet the requirements and assumptions for standard (parametric) statistical methods, non-parametric methods are sometimes useful. Non-parametric methods utilize the ranking of the data values, rather than the individual data values themselves. No assumptions regarding the distribution of the data are required for non-parametric methods (Mendenhall and Beaver 1994). Several of these methods do require a minimum number of samples to be applicable, and these requirements should be reviewed during the sampling planning stages. Among them are the Mann-Whitney test for comparison of the means and variances of two independent samples, the Sign Test for Paired Observations which can be utilized to determine if values of a selected parameter are greater in one sample than in another (the non-parametric paired t-test, which has a binomial distribution under certain conditions), and the Kruskal-Wallis H-test which is used for determining whether multiple samples come from the same population (the non-parametric analysis of variance test, which has a chi-square distribution under certain conditions).

The primary utility of parametric and non-parametric methods is to determine if there is a statistically significant difference between samples or sample means. These tools may be useful in interpreting the data and extending it to unsampled areas. Before getting to that point however, a sampling plan that will produce data lending itself to statistical analysis must be

developed. The key questions in developing a sampling plan are where to sample, how many samples to take, what size samples are required, and what parameters to analyze. The first two questions can be addressed statistically. The latter two are addressed in Olin-Estes and Palermo (2000a).

Developing a Sampling Plan Using Statistical Methods. Statistical packages have been developed to assist in design of sampling plans and/or identification of hot spots that could be adapted to determine the number and location of samples required to characterize a CDF. The STATSS (Statistical Techniques Applied to Sediment Sampling) is a guidance document prepared for the U.S. EPA, Region 5 (Lubin, Williams and Lin 1995) and describes statistical considerations of sampling, and approaches for determining grid and sample size for sampling sediments within a waterway. The Groundwater Modeling System (GMS) is another statistically based package designed to facilitate definition of subsurface contaminant plumes. The following is a general discussion of the underlying statistical principles and data analysis methods which provide the framework for statistically based sampling. The reader is referred to the aforementioned statistical packages and reference for more in-depth guidance in applying these principles.

Where to Sample. There are three basic sampling approaches[2]

- Judgmental approach
- Random approach
- Systematic approach

A judgmental approach involves applying what is known about a site, and sampling in those areas that appear most likely to be contaminated or otherwise of interest. The judgmental approach is essentially the prescriptive approach described in Olin-Estes and Palermo (2000a). A systematic approach involves imposing a uniform grid over the area of interest and sampling from the same location in each grid. A random approach involves selecting sampling points within a gridded area using a random number generator to choose from among the alternative sample locations. The random approach is optimum from a statistical standpoint but, in environmental sampling, may not be the best choice. If the number of samples being taken over a large area is small, purely random sampling could well miss an area of known contamination. The judgmental and systematic approaches help to compensate for this, but may violate the assumption of randomness required in statistical analysis. In practice, the three principal sampling approaches that are used in environmental sampling incorporate a combination of the above elements:

- Systematic random
- Systematic judgmental
- Judgmental random

As previously mentioned, a uniform grid is imposed over the area to be sampled in the systematic methods. In the systematic random method, a random number generator is then used

[2] Personal communication, 9 October 1998, Dr. John H. Pardue, Department of Civil and Environmental Engineering , Louisiana State University, Baton Rouge, LA.

to pick the locations within the grid that are to be sampled (Figure 4-2). Alternatively, one may select only every nth member from the sampling grid with the starting element randomly selected (Lubin, Williams and Lin 1995). Systematic judgmental methods focus attention on the area most likely to be contaminated, a grid is imposed, and a sample is taken from the center of each grid (Figure 4-3). The judgmental random method involves separating the area of interest into blocks that are expected to contain similar samples (such as similar levels of contaminants). A grid is imposed over these areas and sample sites are selected randomly within each block (Figure 4-4). This is also referred to as stratified random sampling (Lubin, Williams and Lin 1995). The sampling method will ultimately be determined by the method that gives the greatest confidence in capturing representative data, quality and availability of existing information on which to base the method selection, and by cost considerations. Additional discussion can be found in U.S. Environmental Protection Agency/U.S. Army Corps of Engineers (1995).

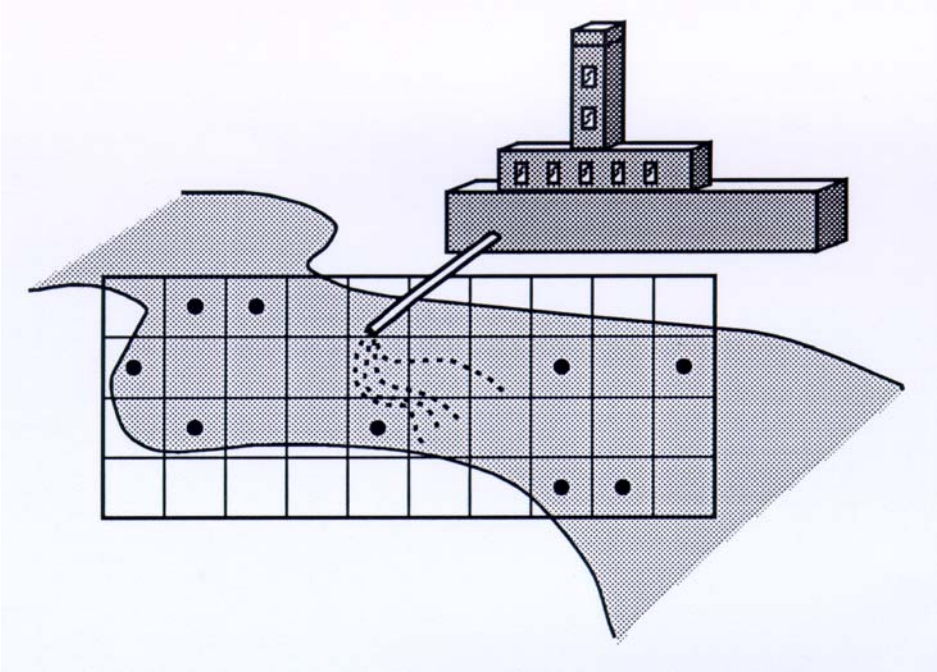

FIGURE 4-2. Systematic random sampling.

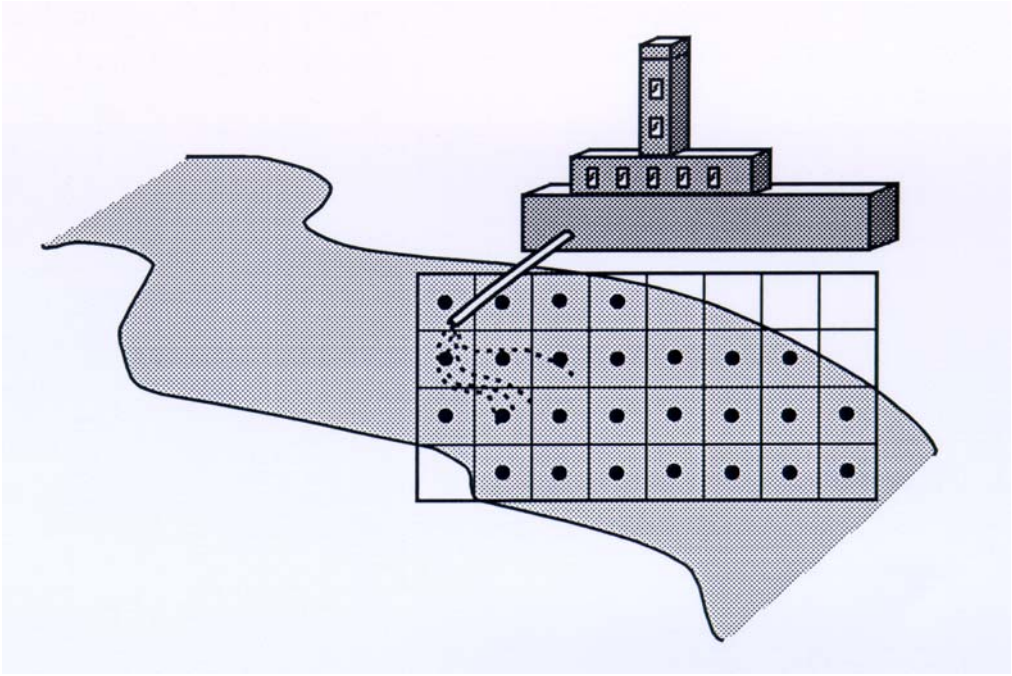

FIGURE 4-3. Systematic judgmental sampling.

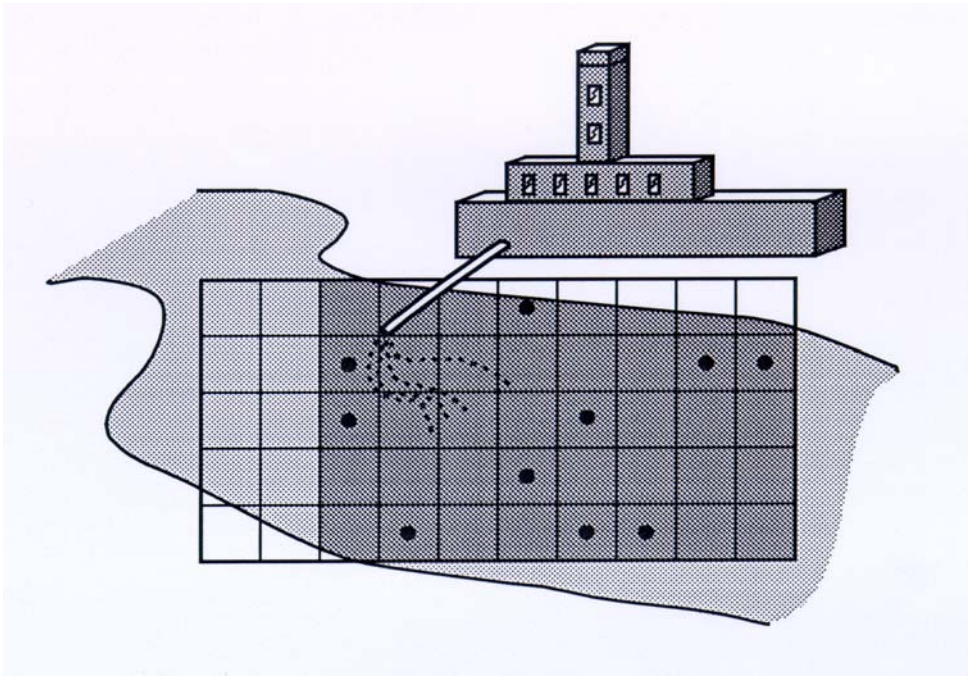

FIGURE 4-4. Judgmental random sampling.

As previously mentioned, a uniform grid is imposed over the area to be sampled in the systematic methods. In the systematic random method, a random number generator is then used to pick the locations within the grid that are to be sampled (Figure 4-2). Alternatively, one may select only every nth member from the sampling grid with the starting element randomly selected (Lubin, Williams and Lin 1995). Systematic judgmental methods focus attention on the area most likely to be contaminated, a grid is imposed, and a sample is taken from the center of each grid (Figure 4-3). The judgmental random method involves separating the area of interest into blocks that are expected to contain similar samples (such as similar levels of contaminants). A grid is imposed over these areas and sample sites are selected randomly within each block (Figure 4-4). This is also referred to as stratified random sampling (Lubin, Williams and Lin 1995). The sampling method will ultimately be determined by the method that gives the greatest confidence in capturing representative data, quality and availability of existing information on which to base the method selection, and by cost considerations. Additional discussion can be found in U.S. Environmental Protection Agency/U.S. Army Corps of Engineers (1995).

Estimating the Number of Samples Required. Ultimately, the number of samples obtained will be determined by cost considerations. The upper threshold will almost certainly be set by the number of samples required to determine the desired parameter (e.g., contaminant concentrations, percent sand) with a specified degree of confidence. If we are able to assume a normally distributed sample, we know from the empirical rule that approximately 95 percent of the values will lie within 1.96 s of the mean, where s is the standard deviation of the sample. An acceptable margin of error can then be used to estimate the number of samples required. For example, if we wish to know the mean concentration of a constituent at a selected depth within 10 mg/kg at the 95-percent confidence level, then:

$$1.96 \frac{s}{\sqrt{n}} = 10 \qquad (4\text{-}1)$$

Solving for *n* gives the number of samples required to determine the mean within 10 mg/kg, at the 95-percent confidence level. Higher or lower confidence levels can be utilized. Further discussion can be found in Mendenhall and Beaver (1994). The obvious disadvantages to this method are that some idea of the variability of the data to be obtained is required prior to sampling. One could utilize results from analysis of selected samples taken within the CDF to estimate s and determine how many additional samples should be analyzed. (The standard deviation for the subsample can be calculated directly, or the range of the data can be utilized to estimate s. If no data is available, an action level can be utilized as an estimated value for the variance. Such an iterative approach is described by Lubin, Williams and Lin (1995), utilizing a mathematical relation for estimating sample numbers that does not utilize the mean, but does incorporate acceptable error levels (α and β). However, environmental data is typically highly variable (large *s*), which may result in unrealistically high numbers of samples required. Additionally, these approaches require the assumption of a normal distribution, which is not typical of most environmental data. The geometric alternative variance can be used to estimate required sample size for lognormally distributed data; this approach is further described in Lubin, Williams and Lin (1995). Another alternative is to sample sequentially, evaluating data as it is generated and continuing to sample until a definitive threshold is achieved at a desired confidence level. The sequential approach and additional methods for estimating required

sample numbers for different grid configurations and confidence levels are described in Lubin, Williams and Lin (1995).

Several of the non-parametric data analysis methods require a minimum number of samples and observations to be valid, or require equally paired numbers of observations between samples to be compared. For example, the Kruskal-Wallis H-test (non-parametric ANOVA) requires at least three samples with at least three observations per sample. When there are more than six observations per sample, the distribution of the H statistic is well approximated by the chi-square distribution (McBean and Rovers 1998). The STATSS (Lubin, Williams and Lin 1995) guidance document provides simple guidance for determining the number of samples required for a specified error level or confidence interval.

Sample Size Required. This is distinct from statistical sample size; in this instance sample size refers to the volume of material that is homogenized and then sampled for analysis. For example, if a 1.8-m (6-ft) core is taken, it will normally be subdivided into smaller sections which are thoroughly homogenized and then a very small subsample of each homogenized section is taken for chemical analysis. Because sediments and the distribution of contaminants within the sediments are typically very heterogeneous, homogenization volume is a relatively important factor in obtaining data that is representative of site conditions. Additional information regarding the influence of sample size and replication in capturing the effects of material heterogeneity is found in Olin-Estes and Palermo (2000a).

Interpreting and Extrapolating (Estimating) Data. Examining the different ways in which available data can be grouped and manipulated in order to reveal trends may be one of the most practical approaches to determining where to sample and how many samples to take. Isaaks and Srivastava (1989) present a clear discussion of a number of methods for grouping data and extrapolating existing data to unsampled points, specifically directed at taking a practical approach to the application of statistical theory. Although many of these methods will be helpful in maximizing the information obtainable from a limited data set, the user should be aware that the results obtained from statistical analysis of the data may differ for different assumptions. Statistical analysis offers an improvement over "best guess" determinations of parameter distributions, but is not a foolproof method. One reason in particular is that the geostatistical methods described by Isaaks and Srivastava (1989) are based on the assumption that the values of interest are spatially continuous. This is probably a reasonable assumption for natural, undisturbed materials over limited areas. For disturbed materials, such as dredged material disposed in a CDF, this is a more difficult assumption to justify. However, the distribution of hydraulically placed dredged material in a CDF is a result of natural processes (settling velocities), assuming the material has not been otherwise disturbed. Under these circumstances, continuity may be a reasonable assumption for limited areas of the CDF. For example, gradation of particle size and contaminant levels would be expected in moving from the inlet area to the outlet of a CDF in which the material is hydraulically placed; two or three distinct zones might be expected.

Interpreting Univariate Data. Data pertaining to a single variable can be presented very simply in a relative location map (Isaaks and Srivastava 1989). For example, if a uniform grid is imposed on the sampling area, and a sample taken from the center of each grid, the resulting value for the parameter of interest can then be superimposed on a map of the area,

giving an indication of spatial distribution. A frequency histogram may also be utilized to give a quick visual on the predominantly occurring values. A cumulative frequency table will be useful in illustrating what percentage of samples fall below a certain threshold; this is a particularly useful technique where contaminant concentrations are of interest. Tests for normality, or lognormality, should be conducted as a matter of routine to establish whether or not the distribution of the data falls within either of these two categories. Typically, environmental data does not, but this should be done as a matter of practice. Summary statistics, including the mean, range, minimum, maximum and standard deviation should be determined for the data, which may be grouped by zones if that provides a more meaningful result. The spatial distribution of values will suggest appropriate groupings, if any.

Parameters of interest in a CDF are likely to include percent sand, percent clay, and contaminant concentrations. The spatial distribution of each of these parameters can be examined individually, but by looking at the relationships between these parameters, it is likely that much can be determined about the material distribution within the CDF using physical parameters and more limited, targeted, chemical analysis. Bivariate data analysis methods provide the means to do this.

Interpreting Bivariate Data. Bivariate data analysis methods permit the comparison of two parameter distributions to determine whether a functional relationship exists between them (Isaaks and Srivastava 1989). Likely to be of interest in determining the distribution of recoverable materials in a CDF is the relationship of percent sand and percent clay to contaminant levels. Summary statistics and tests for normality should be calculated for each distribution individually. A relative location map can be employed, as for the univariate data, giving the values of each parameter as a function of spatial distribution. A scatterplot of the two parameters, one plotted on the ordinate and the other on the abscissa may illustrate any functional dependence that exists. The linearity of the relationship of the variables can be evaluated using the correlation coefficient (ρ). The correlation coefficient varies between –1 and +1; +1 indicates a straight line with a positive slope (positive correlation), -1 indicates a straight line with a negative slope (negative correlation) and values near zero indicate little or no correlation between the variables (Isaaks and Srivastava 1989). For example, one would expect particle size and contaminant concentration to be negatively correlated and percent clay and contaminant concentration to be positively correlated; contaminant level decreasing with increasing particle size. If the correlation coefficient is unduly influenced by a few extreme values, the rank correlation coefficient may be a more useful statistic. This is further described in Isaaks and Srivastava (1989).

Censored Data. In environmental sampling, a high percentage of samples may have no measurable contaminants (non-detects). Concentrations of these analytes, known as censored values, are normally reported as less than the method detection level (<MDL). The actual concentration of the contaminant lies somewhere in the range from zero to the MDL. There are several approaches to handling censored values. One approach is to ignore these values, which results in an overestimate of the mean and underestimate of the standard deviation (McBean and Rovers 1998). This alternative is acceptable only when the number of non-detects is very small. Alternatively, the censored values can be assumed to be equal to the detection limit, but this also introduces bias into the summary statistics. This alternative is preferred when the values are not highly variable and are near the MDL. A third alternative is to assume the censored values to be

equal to MDL/2; this is the preferred alternative when the contaminant is present in highly variable concentrations. There are a number of statistical methods, parametric and non-parametric, for dealing with censored data; these are further described in McBean and Rovers (1998).

Spatial Analysis. There are several variations of data groupings possible based on the relative location map previously described. It may be visually instructive to identify the lowest and highest values on the map, or to replace individual data points with symbols based on assignment to certain ranges. An indicator map utilizes only two symbols, designating those data points falling above and below a specified threshold (Isaaks and Srivastava 1989). The indicator map would likely be most useful for visualizing material in a CDF falling within a certain specification. However, a three dimensional representation of the material in a CDF is needed. Different elevations within the CDF could be mapped separately, and vertical sections mapped in the same manner as the areal sections.

Another useful grouping tool is moving window statistics (Isaaks and Srivastava 1989). A uniform grid of data points is divided into subareas, and the mean and standard deviation of the parameters within each subarea are calculated and remapped at the center of the subarea. This results in a location map in which the parameter value trends and variability are easily seen. Overlapping the subareas can address the need for a sufficient number of data points within each subarea to provide reliable statistics (mean and standard deviation) while keeping areas small enough to capture local detail. Overlapping is particularly useful for small or irregular data sets (Isaaks and Srivastava 1989). Contour maps may also provide a useful visual description of material distribution, although their quantitative value may be limited where extensive interpolation is required. Plots of standard deviation versus sample means, h-scatterplots, correlation functions, covariance functions and variograms are other available interpretive tools (Isaaks and Srivastava 1989) that might be considered if the basic summary statistics do not reveal a meaningful trend.

Estimating Data. Estimating parameters for unsampled locations based on a limited data set is central to environmental characterization problems. A number of methods have been developed under the umbrella of geostatistics that potentially have application. All are subject to the same inaccuracies as a result of site variability. Local estimates based on data that is highly variable are not likely to be very accurate, and should be interpreted in light of the confidence associated with the data set and the degree of spatial continuity evidenced by the data set.

The first step in estimating is to define the problem. The following three features of an estimating problem are adapted from Isaaks and Srivastava (1989):

- Is a global or local estimate desired?
- Do we want to estimate the mean or the complete distribution of data values?
- Do we want point estimates or block values?

In characterizing the deposits within a CDF, we will most likely need some point estimates to identify extreme values (particularly with respect to contaminant levels), mean block values for particle size, and some estimate of the variability of the data, in order to estimate recoverable volumes of material.

All of the methods discussed in Isaaks and Srivastava (1989) involve weighted linear combinations of the known data points:

$$estimate = \hat{v} = \sum_{i=1}^{n} w_i v_i \qquad (4\text{-}2)$$

where

$\hat{v}$ = the data point being estimated
w_i = a weighting factor
v_i = a data value

In estimating, adjustments are made to the sample weighting factor for distance from the point being estimated, and clustering of data points. Samples closest to the data point being estimated will be given more weight than those at a greater distance. Data points that are clustered close together, rather than uniformly distributed over an area, will be given less weight because they are not representative of the larger area and may unduly influence the value of estimated global parameters. Isaaks and Srivastava (1989) describe a number of two and three dimensional declustering approaches. Additionally, closely spaced samples having similar values contain redundant information, and sample weights should also be adjusted for this factor.

An important point to note is that distributions estimated from data points are volume dependent (Isaaks and Srivastava 1989); that is, if a homogenized 0.3-m (1-ft) section of core constitutes a single data point, the distribution estimated with this and like data points constitutes the distribution of parameter values for homogenized 0.3-m (1-ft) core sections. For our application, however, we are really interested in parameter values for larger volumes of a scale that can be practically and economically excavated. Estimates of recoverable materials based on core analysis may not reflect the averaging that occurs when the material is excavated in larger volumes. Correcting for the error introduced by extrapolating small volume estimates to large volumes is a difficult problem, but some effort should be made to evaluate the potential effect of this factor. One approach might be to examine the standard deviation of the means of individual core sites.

Geostatistical estimating methods require identification of a model upon which the estimates are based (Isaaks and Srivastava 1989). A deterministic model can be used if enough is known about the process effects being measured to quantify them. For example, Stokes' law might be used to model the expected distribution of grain sizes across a portion of a CDF based on settling velocities, and extrapolate between data points to estimate the location of transitions across a certain grain size threshold (Note that Stoke's law applies only to discrete settling of individual, non-flocculating particles. Discrete settling of fines does not normally occur in a CDF, thus the model would only be applicable to the coarse material in the CDF.) However, it is unlikely that most CDFs have been operated in a manner consistent enough to utilize this approach. Probabilistic models are utilized when no suitable deterministic model is available; in this approach the sample data are viewed as the result of some random process (Isaaks and Srivastava 1989). The most common parameters utilized in probabilistic approaches are the mean, or expected value, and the variance.

Global estimation is the determination of mean parameter values for large areas. Point estimation is the estimation of parameter values for small areas, or specific locations (Isaaks and Srivastava 1989). Declustering methods are used in both global and point estimation, when samples are clustered rather than distributed over the entire area of interest. Point estimation methods also require weighting of sample values to reflect the relative distance from the point or area being estimated. Two point estimation methods, polygons and the local sample mean method, are adaptations of inverse distance declustering methods. In the polygonal method, the sample value closest to the point we are estimating is selected as the estimate. This value holds throughout the polygon of influence constructed around the estimated point. This method results in discontinuous parameter distributions over the area of interest (Figure 4-5).

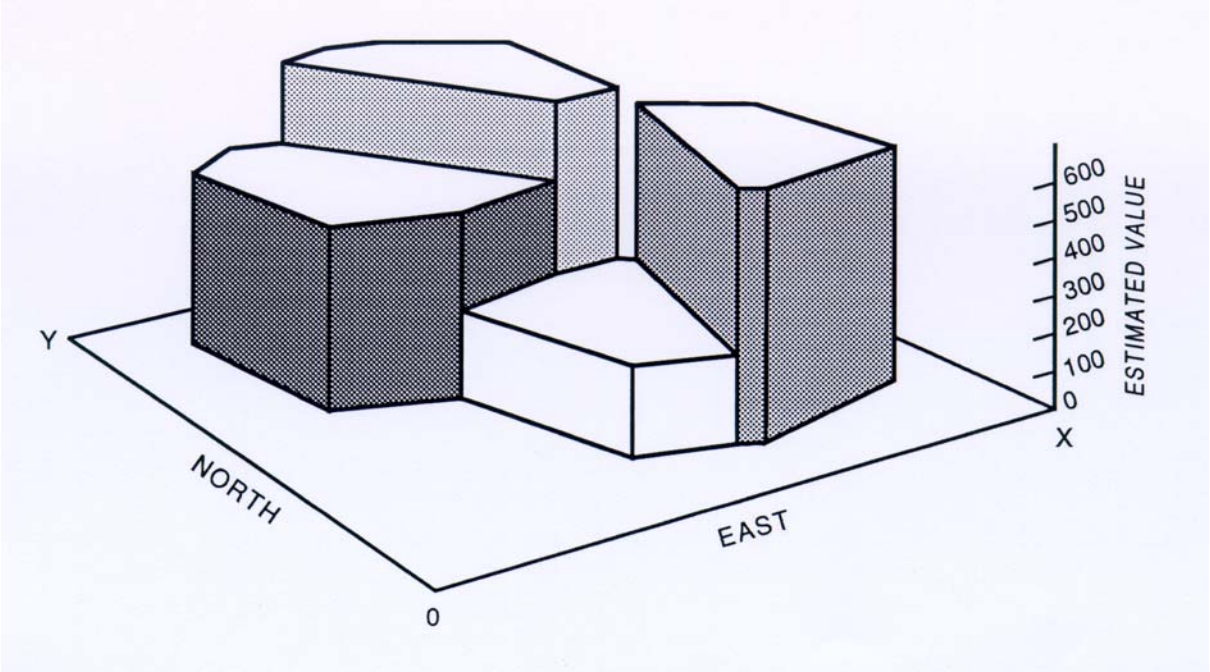

FIGURE 4-5. Polygonal point estimating (adapted from Isaaks and Srivastava 1989).

The method of triangulation eliminates these discontinuities by fitting a plane through three samples surrounding the point to be estimated. An equation of the plane is developed which can be solved for the estimated parameter value at any point within the triangle by substituting the coordinates of the point. Alternatively, weighting factors can also be derived using triangulation. Inverse distance methods apply a weighting factor to nearby samples that is inversely proportional to the distance of the data point from the point being estimated. Some power (p) of the distance may also be used; small values of p decrease the difference in the weighting factors and larger values of p increase the difference. These methods are more fully described in Isaaks and Srivastava (1989).

Selection of nearby samples used as the basis for point estimation is also an important step in the estimating process, and may also be a consideration in location of initial sampling points. Isaaks and Srivastava (1989) refer to areas containing relevant samples as “search neighborhoods”. Within the search neighborhood there must be a sufficient number of nearby

samples, but not too many or redundant samples. The relevance of samples falling within the search neighborhood should also be considered. The number of samples to include is particularly important to inverse distance and kriging. The number of samples included using geometric estimating techniques is self-determining, based upon the orientation of the samples.

Normally, all available samples within the defined search neighborhood are used in estimation. Typically, an ellipse is centered on the point being estimated, with the long axis oriented in the direction of greatest continuity of the sample values (Isaaks and Srivastava 1989). In a CDF, this would likely be horizontally across the cell, perpendicular to the direction of flow. The length to width of the ellipse is determined by judgment, based on the degree of anisotropy evidenced in the available data.

Alternatively, all samples within a specified distance of the point to be estimated might be used. For regularly gridded data, the search neighborhood should be at least large enough to include the four nearest samples. In practice, a minimum of 12 samples is typical (Isaaks and Srivastava 1989). The search neighborhood for irregularly gridded data should be just larger than the average spacing between the sample data, estimated as follows (Isaaks and Srivastava 1989):

$$Average\ spacing\ between\ samples = \sqrt{\frac{Total\ area\ \mathrm{cov}ered\ by\ samples}{Number\ of\ samples}} \qquad (4\text{-}3)$$

At the same time that one must be concerned with having a sufficient number of samples for estimating, too many samples can be problematic. Computations for estimating procedures such as kriging become cumbersome with too many samples. This can be addressed by compositing samples outside the immediate area of the point being estimated. This procedure is further described in Isaaks and Srivastava (1989).

Ordinary kriging is an unbiased estimating method that is intended to minimize the mean residual m_R, or error, and the variance σ^2_R of the errors. A probability model in which the bias and the error variance can be calculated is used, and nearby samples weighted to give m_R=0 and minimize σ^2_R. The sample weights will change as unknown values are estimated (Isaaks and Srivastava 1989). The weighting matrix w is derived by multiplying two matrices (C and D) constructed from a selected random function model and parameters. The mathematical development of this procedure is somewhat complicated and the relationship to the physical problem not readily apparent. Simply described, the matrices are composed of the covariances between sample data points and the point being estimated. The D matrix (Isaaks and Srivastava 1989) "provides a weighting scheme similar to the inverse distance methods"; the covariance between any sample and the point estimated decreases as the distance between them increases. The difference between the D matrix and inverse distance weights is that the covariances can be calculated from a larger family of functions, rather than being limited to a single form $|h|^{-p}$ (where h is the distance between the points and p is an arbitrarily selected exponent, as previously described). In effect, the kriging distance can be considered a statistical distance, rather than the geometric distance of the inverse distance methods (Isaaks and Srivastava 1989). The C matrix takes into account spatial continuity and redundancy, automatically providing an adjustment for clustering of data points. Ordinary kriging is, therefore, less adversely affected by sample clustering than other estimating methods, although it is computationally more difficult.

One characteristic of ordinary kriging is that, for selected functions, some of the sample weights may be negative, although the sum of the sample weights will always be 1, a necessary condition of unbiasedness. The result is that the procedure can yield estimates larger than the largest sample value and smaller than the smallest sample value. Since the data set is unlikely to contain the most extreme values, this is advantageous. A disadvantage is that negative estimates may also result. These may be arbitrarily set to zero when negative values do not make physical sense, as in the case of concentrations (Isaaks and Srivastava 1989). Selection of an appropriate model and model parameters requires fitting available data with a suitable function. This procedure, and the result of varying the function parameters, is extensively discussed in Isaaks and Srivastava (1989). Additionally, the random function model can be selected to reflect the degree of anisotropy of the site. Obviously, judgment and experience are requisite to utilizing this procedure.

Other methods of point estimation can be found in Isaaks and Srivastava (1989). While ordinary kriging provides a method of obtaining point estimates, block kriging is a procedure for estimating an average value within a prescribed block. The previously described estimating methods utilize the spatial continuity of a single variable to provide estimates for unsampled points. Cokriging is a method that utilizes information from secondary variables, which may be correlated with the primary variable, to improve estimates. An example of this might be the use of grain size as the secondary variable to improved estimates of contaminant concentration, the primary variable.

The assistance of a statistician will undoubtedly be helpful in designing a sampling plan that will produce data suitable for statistical analysis and estimating procedures. The forgoing is only a general discussion of the procedures and major considerations; a thorough familiarity and understanding of the procedures by the practitioner is warranted.

COMPLETION OF BU AND SEPARATION FEASIBILITY EVALUATION

Once a reliable estimate of material recovery potential has been developed, the information can be used in completing the evaluation of BU and separation feasibility. If recovery potential matches the requirements for the BU applications under consideration, and separation is required, appropriate operational methods or equipment for separation are selected. A cost analysis can then be performed and the final decision on separation feasibility made. Procedures for equipment selection and cost estimating are described in USEPA (1999). If separation is not required, a more straightforward cost benefit analysis can be conducted.

CONCLUSIONS

Development of a re-use plan for a CDF or dredging project will require a multi-step approach incorporating existing data, practical and/or statistical sampling approaches, and identification of local beneficial use opportunities and requirements. Little field verification is presently available regarding the efficacy of one sampling approach over another in characterizing the distribution of materials in a CDF. As further field experience is gained, refinements can likely be made that will result in an optimal approach and greater confidence in the results. Physical separation is only one of several approaches that can be taken to produce material suitable for various beneficial uses. Separation should be evaluated together with other alternatives to determine the most suitable approach for a given site.

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CHAPTER 5

FRACTIONATION STUDY OF NATURAL SEDIMENTS FOR DETERMINING PAH AND PCB DISTRIBUTION – PART 1: PAHS

INTRODUCTION

The fate of contaminants mobilized from sediment during dredging and disposal is of concern in Section 404 (Clean Water Act) evaluations (USEPA/USACE 2004). To demonstrate compliance with water quality standards and assess the need for mixing zones or mitigation measures, the magnitude of contaminant release resulting from a dredging action is evaluated for applicable contaminant exposure pathways (USEPA/USACE 1991, 1998; USACE 2003). Additionally, because disposal space for dredged material is becoming more limited in some areas of the United States, alternative management practices are increasingly being considered (Great Lakes Commission 2004; Price et al. 1997). Separation of relatively clean fractions of the sediment for beneficial use reduces the amount of dredged material requiring confined disposal (Olin-Estes and Palermo 2001).

Contaminant partitioning and distribution are central to alternatives analysis (USEPA/USACE 1991, 1998; USACE 2003). Effluent quality, for example, is based upon evaluation of contaminant solubilization under two boundary conditions: 1) mixing of sediment pore water and the overlying carrier water, and 2) equilibrium between sediment, pore water and carrier water. Equilibrium calculations require knowledge of the partitioning behavior of the contaminants of concern. Theoretical partitioning coefficients may be developed based on site specific sediment and contaminant properties (Hansen et al. 1999; Brannon et al. 1998; Chiou, McGroddy and Kile 1998; DiToro et al. 1991; Pardue et al. 1993), values may be obtained from published references, or an observed coefficient may be calculated from sediment and pore water data (EPA 1999). Disparity of theoretical and observed partitioning coefficients may be as much as an order of magnitude or more, however (Kan et al. 1998). These differences may be resolved and representative values selected by taking into account other available information, such as the results of an elutriate test (Palermo 1986). Alternatively, the most conservative values may be selected for the analysis. Fractionation studies may also be conducted to evaluate the association of contaminants with specific size or density fractions of sediments, to assess the feasibility of separation for contaminant reduction or suitability of material for beneficial use, (Olin-Estes and Palermo 2001).

PAHs are hydrophobic organic compounds commonly found in sediments of navigation waterways (National Research Council 1997; USEPA 1993). PAHs are ubiquitous compounds that may be generated as a byproduct of incomplete combustion of organic materials (pyrogenic), may be commercial products introduced to the environment in industrial and wastewater discharges, or may be associated with crude oil (Thorsen, Cope and Shea 2004). The source of PAHs is an important factor in the mobility and bioavailability of the compounds. Petrogenic (petroleum) PAHs are dominated by low molecular-weight compounds, with a greater abundance of methylated derivatives than parent compounds. Pyrogenic PAHs are typified by high molecular-weight compounds (more than four rings) with parent PAHs being more abundant than methylated compounds (Depree et al. 2004). PAHs are relatively insoluble and are typically

associated with particulates, humic matter, or oily matter in soils and sediment (Tox Probe Inc. 2002). PAHs have a high affinity for soot, and pyrogenic PAHs may be co-produced with (a component of) soot.

Sorption to organic matter is reportedly more significant for PAHs than for PCBs, which is attributed to a high affinity for the aromatic structures in organic matter (Chiou, McGroddy, and Kile 1998) and the planar configuration of PAHs, which reduces steric effects (Gauthier et al. 1987; Chin et al. 1997, as cited in Müller et al. 2000). While the presence of high levels of dissolved organic carbon has been shown to increase the apparent solubility of PCBs (Brannon et al. 1998; Hwang et al. 1998), DOC composed of aliphatic carbon (non-aromatic) has been shown to be less important than soil organic matter and clays in sorption of PAHs (Hwang and Cutright 2004).

The major objectives of this research effort were to ascertain the distribution trends of PAHs in three natural sediments and to evaluate the potential usefulness of fractionation studies to treatability and fate and effects evaluations. Fractionation studies offer a vehicle to evaluate the association of contaminants with specific phases of sediments and to establish correlations to those phases from which more global partitioning coefficients might be derived. This research effort was developed to meet the dual objectives of developing simple bench scale testing methods for separation feasibility evaluations and laying a foundation for improved understanding of the target phases important to contaminant reduction.

MATERIALS AND METHODS

Sediments and Analytes. Materials employed in the separation study included one freshwater and two marine sediments[1]. The freshwater sediment was obtained at the offloading point to the CDF for Calumet River. The marine sediments were taken directly from the harbors in New York and New Bedford. Sediments were packaged in 5-gallon HDPE buckets and maintained at 4°C during transport and while in storage.

Sediments were homogenized in a large stainless steel mixer when received at the laboratory. Aliquots of homogenized sediment were tested to determine specific gravity of solids (MD0302), moisture content, grain-size distribution (ASTM D422), classification (ASTM D2488), fraction organic carbon (ASTM D2974), cation exchange capacity (CEC) (SW-846 Method 9080/9081), pH (SW-846 Method 9040B), and fraction expandable clay (x-ray diffraction). Soot analysis was conducted using the procedure reported in Gustafsson et al. (1997), which is essentially a modification of the acidification and combustion procedure used for TOC determination (SW-846 9060). Samples were also analyzed in duplicate for selected analytes, using SW-846 methods. These samples were packaged in amber glass jars with Teflon® lids and maintained at 4ºC without preservatives prior to analysis. Analytes selected included PAHs typically found at measurable concentrations in navigation sediments, including: acenaphthene, acenaphthylene, anthracene, benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[g,h,i]perylene, benzo[k]fluoranthene, chrysene, dibenzo[a,h]anthracene, fluoranthene, fluorene, indeno[1,2,3-c,d]pyrene, 2-methylnapthalene,

[1] The study samples were taken from well-known harbors with the specific objective of obtaining materials containing sufficient contaminant levels to facilitate testing. They were obtained as grab samples from a single location or limited area, and do not necessarily represent the character of the materials in these water bodies as a whole.

naphthalene, phenanthrene, pyrene. Sediments were also analyzed for oil and grease (O&G), and total organic carbon (TOC).

Samples of pore water were obtained by centrifuging homogenized sediment. Pore water was analyzed for the same constituents as the sediments, as well as dissolved organic carbon (DOC). Due to volume limitations, no replicate analyses were obtained for PAHs in pore water.

Density Separations. A solution of non-toxic, water-soluble sodium polytungstate was used for the density separations. The heavy media was made up to give a solution density of 2.0 g/cm^3 when mixed with the sediment, adjusting for expected dilution from pore water in the sediment sample. In order to prevent formation of a calcium precipitate in the media, calcium ions were removed from the sediment by saturating the sediment with a 1N Sodium Acetate solution at a 6:1 water:sediment ratio. This was tumbled overnight and then centrifuged, and supernatant decanted. The procedure was repeated once with sodium acetate and again with distilled, de-ionized water (DDI), to remove the sodium acetate.

Samples of pretreated bulk sediment were placed in 250 ml Nalgene centrifuge bottles with the solution of sodium polytungstate. Samples were sonicated briefly in a water bath to encourage separation of the different density materials and then centrifuged until a clear separation of phases occurred. The light (organic) fraction was decanted onto a microfiltration apparatus and rinsed with DDI water to remove residual heavy media. Initially, filters used were Whatman GF/F Glass Microfibre Filters (0.7 µm). Because solids were difficult to remove from these filters, Lida 0.45 µm nylon filter membranes were later substituted. Filtration through the nylon filters was slower, but removal of solids from the filters was less problematic. The heavy (mineral) fraction was recombined with additional sodium polytungstate and the procedure repeated until no further organic phase could be separated from the mineral phase. The heavy fraction was then recombined with DDI water, sonicated, centrifuged and decanted through a microfiltration apparatus to remove residual heavy media. Samples from each density fraction were analyzed on the Coulter LS 100 particle size analyzer (Beckman Coulter, Inc., USA) to determine particle size distribution.

The density separation was performed once per sediment. Wet solids were collected from the microfiltration apparatus and placed in amber glass jars with Teflon lined lids for chemical and physical analysis. No preservatives were added. Samples were maintained in storage at 4°C. Replicate samples were obtained from the mineral fraction where sufficient material was available. Material volume was insufficient for replicates from the organic fraction.

Size Separations. Size separation of homogenized sediment was accomplished in three stages. A specified amount of wet sediment, sufficient to produce adequate quantities of each fraction, was weighed out and wet sieved through a 4.75-mm sieve and a 200-mesh (75-µm) sieve. Material retained on the coarse sieve was classified as oversize and was not tested. Material retained on the fine sieve was classified as sand. Slurry passing the 200-mesh sieve was diluted to approximately 15 percent solids by weight and processed through a 2-inch Mozely hydrocyclone. Underflow was designated as the operationally defined silt fraction, overflow was designated as the operationally defined clay fraction. Both silt and clay fractions were dewatered using a continuous flow CF 35M Microseparator. Samples from each size fraction were analyzed on the Coulter Counter to evaluate particle size distribution.

The size separation was performed only once for each sediment but, where sufficient quantities of material were available, replicate samples of each operational size fraction were

taken for chemical and size distribution analysis. Wet solids were placed in amber glass jars with Teflon lined lids for chemical and physical analysis. No preservatives were added. Samples were maintained at 4°C.

RESULTS

Physical Characterization. Physical properties of the three sediments are summarized in Table 5-1. Calumet is the coarsest sediment, with a comparatively low organic fraction, classified as a sandy silt (ML), dark gray, trace of gravel (4.7 percent) visual. New Bedford contains the highest proportion of organic materials, followed by New York. Both are classified as sandy silt (ML), dark gray visual. Results of the x-ray diffraction analysis are also summarized in Table 5-1. Quantitative analysis of clays was not possible due to the presence of low angle clays. Basal spacing on air-dry oriented patterns of 14-15.5 Å is indicative of smectite, vermiculite or chlorite. Mixed layer clays, which may be composed of or a precursor to the formation of expansive clays, were also identified. The presence of smectite and mixed layer clays indicates potential for sorption or ion exchange in the clay minerals of all three sediments. Cation exchange capacity was comparable for the three sediments and is indicative of exchange capacity of clays and organic materials in the sediments.

TABLE 5-1. Bulk Sediment Physical Characterization

			X-Ray Diffraction											
Sediment	**Sand/Silt/Clay[a] % by Wt**	**Organic Content %**	**Quartz**	**Plagioclase Feldspar**	**Potassium Feldspar**	**Illite**	**14 angstrom clay**	**Mixed layer clay**	**Calcite**	**Dolomite**	**pH**	**CEC meq/100 g**	**Specific Gravity[b]**	**Moisture Content %**
Calumet	42.2/39.6/13.5	4.3	X			X	X	X	X	X	7.59	7.59	2.71	33.3
New Bedford	35.0/56.1/8.9	8.3	X	X	X	X	X	X			6.65	6.65	2.46	60.5
New York	23.3/50.4/26.3	7.6	X	X			X	X			7.16	7.16	2.64	63.3

[a] Sieve and hydrometer analysis. [b] Specific gravity of solids.

Chemical Characterization. Results of the chemical characterization of the bulk sediments and pore water are summarized in Table 5-2. Sediment PAH concentrations reported represent the mean of two replicates. Pore water results are unreplicated values. Data in this table is raw, unadjusted data. Corrections made to pore water concentrations for sorption losses to centrifuge containers are not reflected here.

Mass Balance. Recovery of all solids for gravimetric mass balance was not feasible due to processing losses and slurry volumes generated in the cyclone separation. The relative distribution of sediment mass to each size and density fraction could be estimated however, based on measured properties of the bulk sediment and the resulting fractions. The procedure was as follows:

TABLE 5-2. Bulk Sediment PAH Analysis

	Calumet		New Bedford		New York	
PAH	**Bulk (µg/kg)**	**Pore Water (µg/l)**	**Bulk (µg/kg)**	**Pore Water (µg/l)**	**Bulk (µg/kg)**	**Pore Water (µg/l)**
2-Methylnapthalene	1840	0.19	183.5	<0.1	149.5	<0.1
Acenaphthene	1260	1.7	171	<0.1	55.2	0.71
Acenaphthylene	442	0.61	29.7	<0.1	21.9	<0.1
Anthracene	3305	0.88	180	<0.1	477	0.16
Benzo[a]Anthracene	5550	0.65	2540	<0.1	774.5	<0.1
Benzo[a]Pyrene	4365	0.52	2485	<0.1	837	<0.1
Benzo[b]Fluoranthene	3655	0.39	2435	<0.1	776.5	<0.1
Benzo[g,h,i]Perylene	2455	0.23	1710	<0.1	556.5	<0.1
Benzo[k]Fluoranthene	2875	0.38	1755	<0.1	558	<0.1
Chrysene	5165	0.59	2460	<0.1	815	<0.1
Dibenzo[a,h]Anthracene	633.5	0.08	373.5	<0.1	124	<0.1
Fluoranthene	10460	2.19	4315	0.1	1400	0.18
Fluorene	2130	1.17	235	<0.1	80.5	<0.1
Indeno[1,2,3-c,d]Pyrene	2550	0.29	1915	<0.1	581.5	<0.1
Naphthalene	10887	0.13	309.5	<0.1	221	<0.1
Phenanthrene	9475	2.53	719	<0.1	1995	<0.1
Pyrene	9325	1.83	5190	0.22	1995	0.21
Sorptive Phases	**(mg/kg)**	**(mg/l)**	**(mg/kg)**	**(mg/l)**	**(mg/kg)**	**(mg/l)**
TOC/DOC	88,217	30	87,053	10	51,317	6.3
O&G	4,215	N/A	4,480	N/A	3,285	N/A
Soot	17,569	N/A	2,967	N/A	9,648	N/A

On a per unit weight wet sediment basis, the amount reporting to the process fractions was estimated as follows:

$$M_W = M_B * M.C. \tag{5-1}$$

where

M_w = mass water (kg)
M_B = wet mass of bulk sediment (kg)
M.C. = moisture content (expressed as decimal)

The mass of the dry solids (M_S) in the sediment was then calculated by difference:

$$M_S = M_B - M_W \tag{5-2}$$

The mass of solids includes all solid phases, including mineral and organic materials.

Estimation of Material Reporting to Density Fractions. The mass of organic material in the bulk sediment is equal to the mass of organic material reporting to the density fractions:

$$f_{OB}M_S = f_{OO}M_{OF} + f_{OM}M_{MF} \quad (5\text{-}3)$$

where

f_{OB} = fraction organics in the bulk sediment
f_{OO} = fraction organics in the organic (SG<2.0) fraction
f_{OM} = fraction organics in the mineral (SG>2.0) fraction
M_{OF} = mass of operationally defined organic fraction (kg)
M_{MF} = mass of operationally defined mineral fraction (kg)

The fraction of organics in the bulk sediment and density fractions (f_{OB}, f_{OO} and f_{OM}) was obtained from the TOC measurement. The mass of the bulk sediment solids (M_S) is equal to the dry mass of the mineral and organic fractions combined:

$$M_S = M_{OF} + M_{MF} \quad (5\text{-}4)$$

This gives two equations (5-3 and 5-4) and two unknowns (M_{OF} and M_{MF}).

Estimation of Material Reporting to Size Fractions. The silt and clay remaining in the sand fraction after separation is assumed to be negligible. The mass of the sand fraction (M_{SAF}) can therefore be simply calculated based on the percent sand in the bulk sediment as follows:

$$M_{SAF} = M_S * f_{sand} \quad (5\text{-}5)$$

where

M_S = dry mass of sediment solids as previously defined (kg)
f_{sand} = percent sand in bulk sediment (particles 75 µm-4.74 mm, dry weight basis), as a decimal

M_{SAF} includes mineral and organic particles reporting to this fraction. The mass of the mineral sand fraction (M_{SA}) can be estimated as follows:

$$M_{SA} = M_{SAF} - M_{OSAF} - M_{SiSAF} - M_{ClSAF} \quad (5\text{-}6)$$

where

M_{OSAF} = mass organics in sand fraction (kg)
M_{SiSAF} = mass silt in sand fraction (kg), assumed to be negligible
M_{ClSAF} = mass clay in sand fraction (kg), assumed to be negligible

The mass of organics in the sand fraction is obtained from the TOC measurement of the sand fraction.

The silt and clay separation results in a distribution of silt and clay size particles, composed of both organics and minerals, to both operationally defined fractions. Because slurry volumes were such that all of the solids could not readily be recaptured by centrifuging, the weight distribution between these two fractions was estimated based on the particle size distribution in representative samples of the fractions and the mass distribution of silt and clay size particles in the bulk sediment. This was done as follows:

The total mass of silt size particles (M_{SI}, organic and mineral combined) is given by

$$M_{Si} = M_S * f_{SiB} \tag{5-7}$$

where

f_{SiB} = percent silt in bulk sediment (5-75 μm particles, dry weight basis), as decimal

Similarly, the total mass of clay size particles (M_{Cl}, organic and mineral combined) is given by

$$M_{Cl} = M_S * f_{ClB} \tag{5-8}$$

where

f_{ClB} = percent clay in bulk sediment (<5 μm particles, dry weight basis), as a decimal

Expressed in terms of the distribution between the silt and clay "fractions", and assuming silt lost to the sand fraction is negligible:

$$M_{Si} = M_S * f_{SiB} = f_{SiSF} * M_{SF} + f_{SiCF} * M_{CF} \tag{5-9}$$

where

f_{SiSF} = fraction silt in silt fraction
f_{SiCF} = fraction silt in clay fraction
M_{SF} = mass silt fraction (kg)
M_{CF} = mass clay fraction (kg)

The fraction of silt and clay in the respective fractions was determined by Coulter counter analysis. Coulter results are given in percent by volume, which must be converted to percent by weight. Assuming the specific gravity for the silt and clay particles is approximately equal based on the physical characterization results, however, percent by volume is equivalent to percent by weight. The corresponding equation for clay is

$$M_{Cl} = M_S * f_{ClB} = f_{ClCF} * M_{CF} + f_{ClSF} * M_{SF} \tag{5-10}$$

where

f_{ClSF} = fraction clay in silt fraction
f_{ClCF} = fraction clay in clay fraction

This procedure gives two equations (5-9 and 5-10) that are then solved for the two unknowns (M_{CF} and M_{SF}). The relative sediment mass reporting to each size and density fraction as estimated by the mass balance procedure (with size fractions and density fractions considered independently of each other) is illustrated in Figure 5-1.

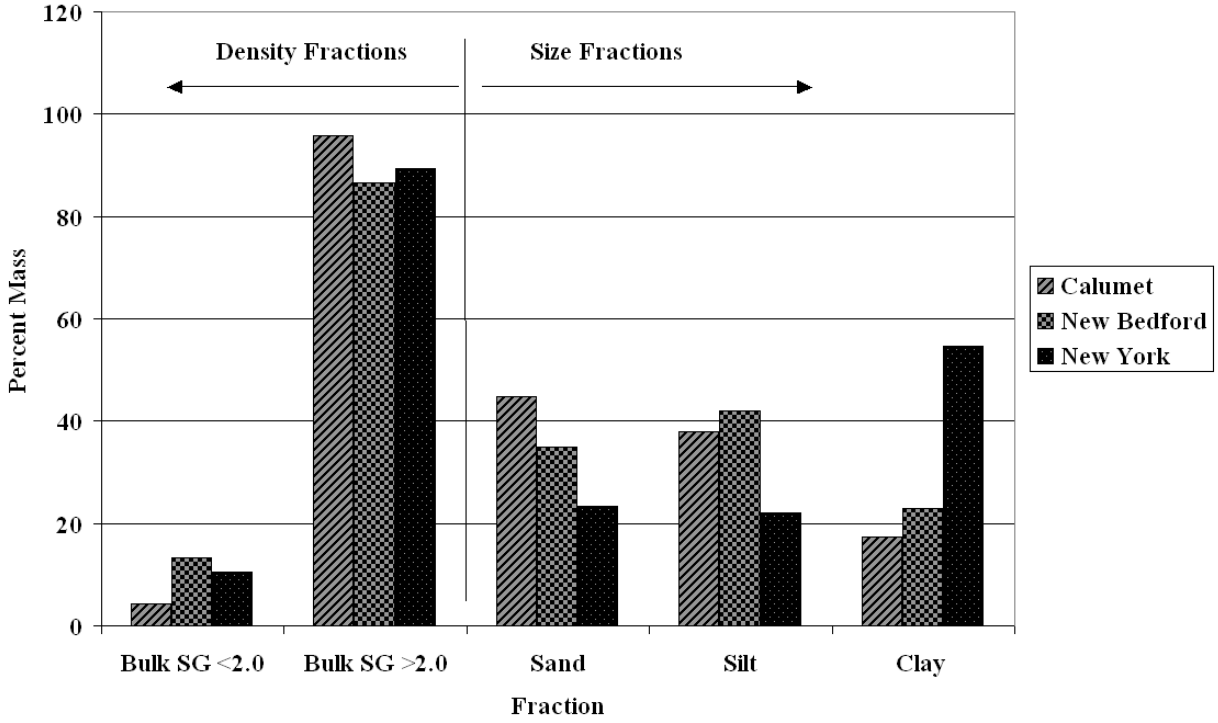


FIGURE 5-1. Percent total sediment mass reporting to size and density fractions.

Particle Size Analysis of Fractions. Samples of the operationally defined fractions were analyzed on the Coulter Counter to assess the effectiveness of the separations. Of particular interest are the differences in clay content over the size fractions and the fate of the clay particles in the density fractions. Because the clay particles are so fine, they are easily entrained with coarser materials. Clay sized organic materials cannot be distinguished from clay minerals based on particle size analysis, however, so an additional measurement was taken on samples from each of the fractions, treated to remove soot and organic carbon. The <5 μm material remaining was presumed to be clay mineral. Samples were heated in a muffle furnace at 350ºC for 24 hours to drive off the organic carbon, and then soot was removed with an additional density separation step. The percent by volume <5.1 μm as measured by the Coulter is given for the bulk sediment and the fractions in Table 5-3, with measurements obtained for the muffled samples in parenthesis. Note that in many cases the volume percent <5 μm is higher rather than

lower after removal of organics and soot. The reason for this is unknown, but may have to do with organic materials binding clays together to form larger "particles", which then disaggregate after the organic carbon is removed.

TABLE 5-3. Particle Size Analysis of Operationally Defined Fractions: Percent by Volume < 5.1 µm (Muffled Samples in Parenthesis)

	Fraction					
Sediment	**Bulk**	**SG <2**	**SG>2**	**Sand**	**Silt**	**Clay**
Calumet	24.9 (22.8)	13.6 (22.7)	32.7 (36.6)	ND[a]	6.8 (7.5)	49.9 (49.0)
New Bedford	16.9 (27.7)	19.4 (25.2)	11.2 (21.6)	1.0 (ND)	7.0 (5.8)	26.1 (29.4)
New York	24.5 (33.9)	10.0 (27.5)	35.2 (29.9)	ND	5.6 (55.1)	43.3 (48.8)

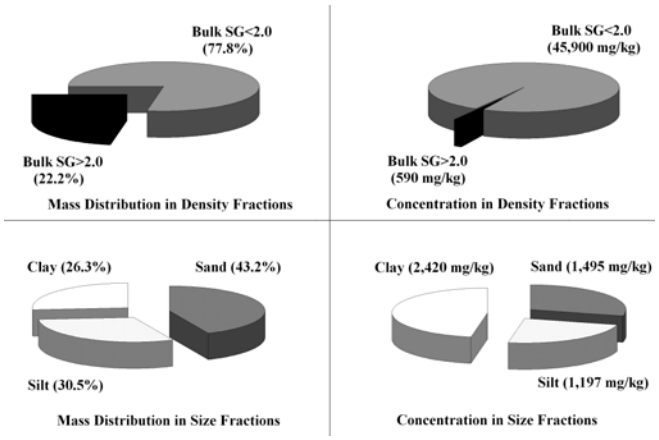
[a] ND: Valid Coulter measurements could not be obtained for the sand fractions of Calumet and New York, or for the muffled sand fraction of New Bedford, due to problems with settling of particles in the instrument lines.

Oil and Grease, Soot and Organic Carbon Distribution. The mass distribution and concentration of oil and grease (OG), soot and organic carbon (OC) in the size and density fractions are illustrated in Figures 5-2, 5-3, and 5-4. Results pictured are from two separate samples taken from homogeneous material, one used for density separation and one for size separation. Organic carbon concentration has been corrected for soot and for oil and grease ($OC = TOC - Soot - OG$). Based on these concentrations, the mass of organic carbon is much larger than either OG or soot (ranging from 1.4 to 82 times as much) in all fractions for all sediments except the organic fraction of Calumet. Here, the mass of soot is approximately 14 times greater than OC.

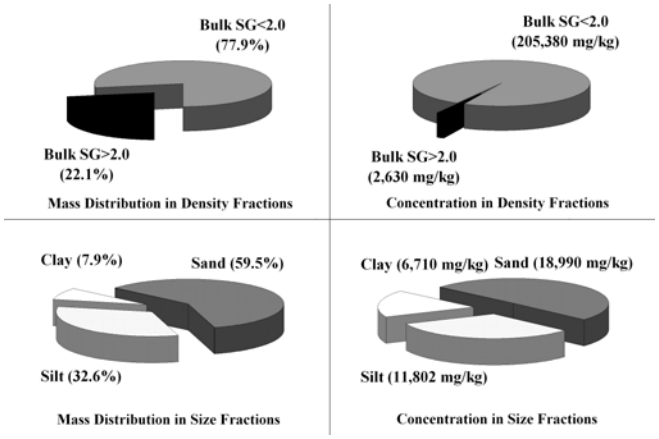
PAH DISTRIBUTION

Calumet. Mean concentration of PAHs was more than an order of magnitude higher in the organic (SG<2) fraction, which comprises 4.3 percent of the sediment mass, than in the mineral (SG>2) fraction (Figure 5-5). In the size fractions, mean PAH concentrations were highest in the clay fraction, comprising 16.7 percent of the sediment mass, followed by sand (44.2 percent of the sediment mass) and then silt (39.1 percent of the sediment mass). This general distribution was representative of all PAHs except acenaphthene, fluorene and naphthalene, which were highest in the sand (Table 5-4).

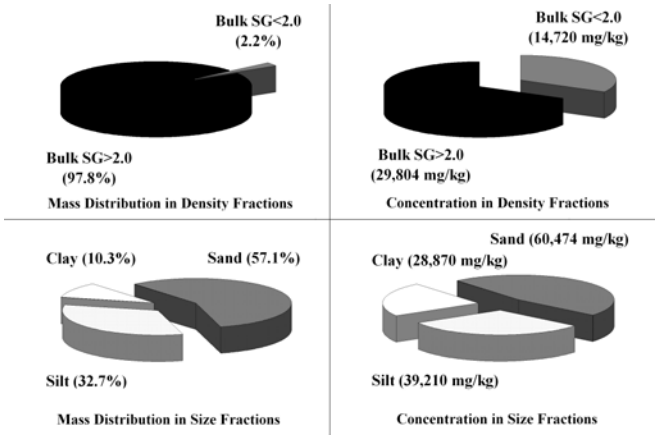
On a mass basis, mean PAH mass is almost evenly split between the density fractions (Figure 5-5). Mass of individual PAHs benzo[a]anthracene, benzo[a]pyrene, benzo[a] fluoranthene, benzo[g,h,i]perylene, benzo[k]fluoranthene, chrysene, dibenzo[a,h] anthracene, and indeno[1,2,3-c,d]perylene were highest in the organic fraction. Fluoranthene and pyrene mass was approximately equal between the density fractions, and the remainder of the PAHs was higher in the mineral fraction (Table 5-4). In the size fractions, mean PAH mass was highest in sand and approximately equal in silt and clay. Individually, all PAHs were higher in the sand fraction. Acenaphthene, acenaphthylene, anthracene, fluorene, 2-methylnaphthalene, naphthalene, and phenanthrene mass was higher in the silt fraction than in the clay. All other PAHs were higher in the clay fraction than in the silt.



a) Oil and Grease Distribution

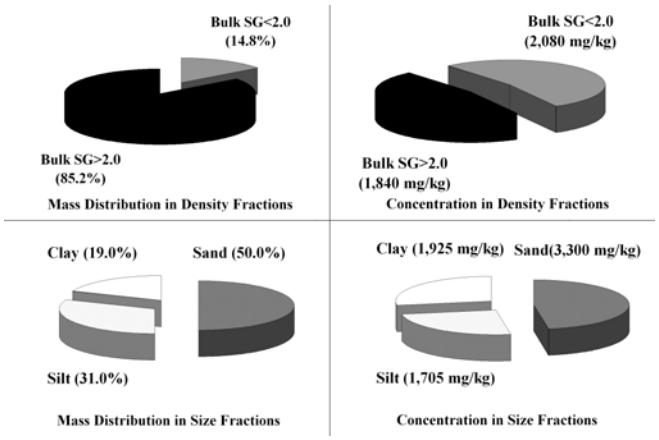


b) Soot Distribution

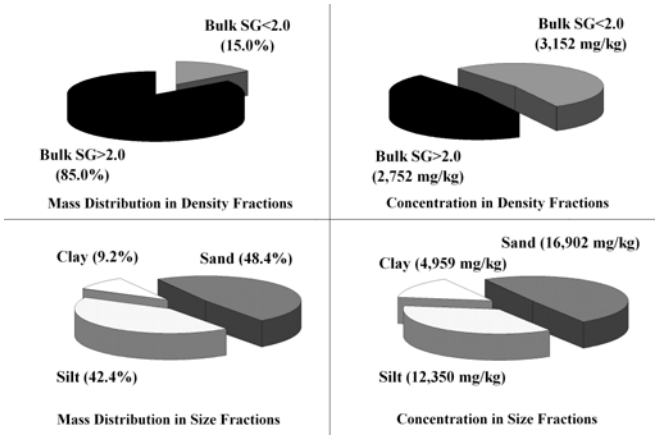


c) Organic Carbon Distribution

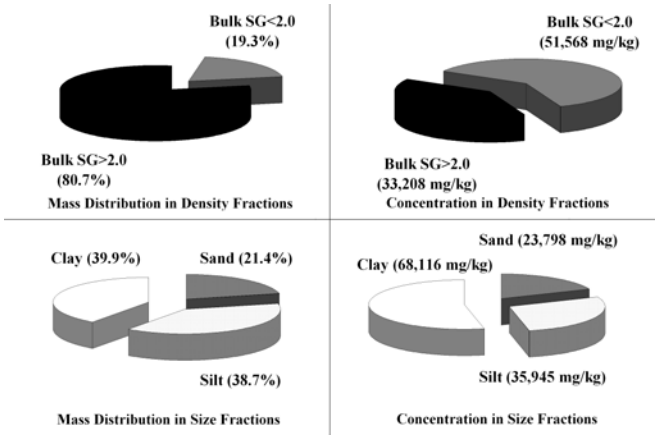
Figure 5-2. Calumet Sorptive Phase Distribution



a) Oil and Grease Distribution

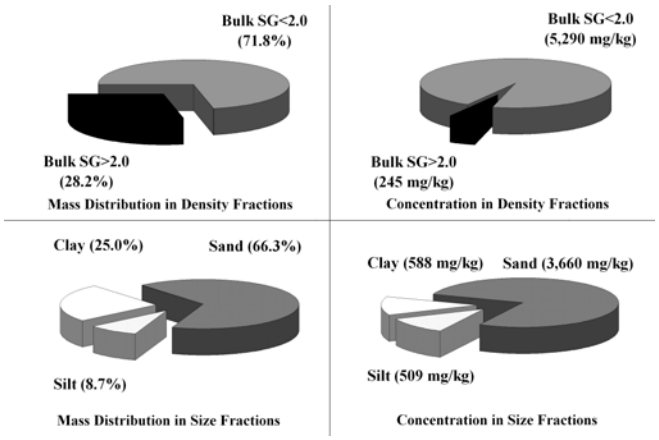


b) Soot Distribution

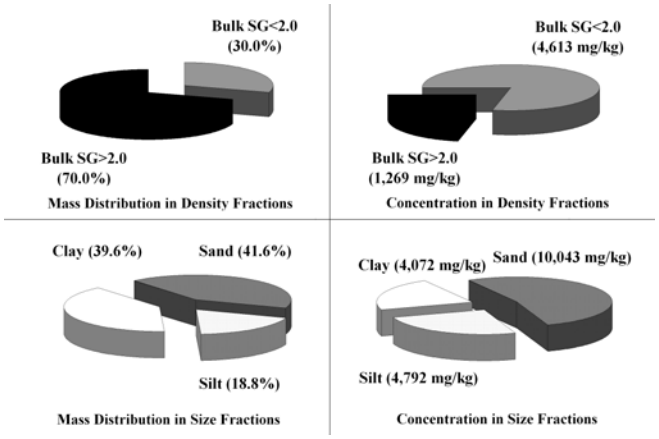


c) Organic Carbon Distribution

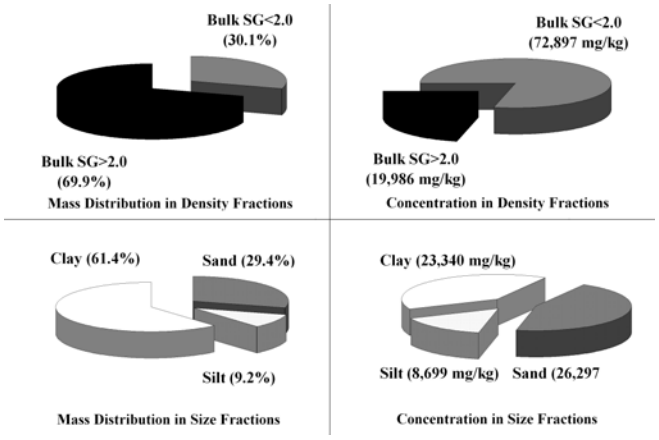
Figure 5-3. New Bedford Sorptive Phase Distribution



a) Oil and Grease Distribution



b) Soot Distribution



c) Organic Carbon Distribution

Figure 5-4. New York Sorptive Phase Distribution

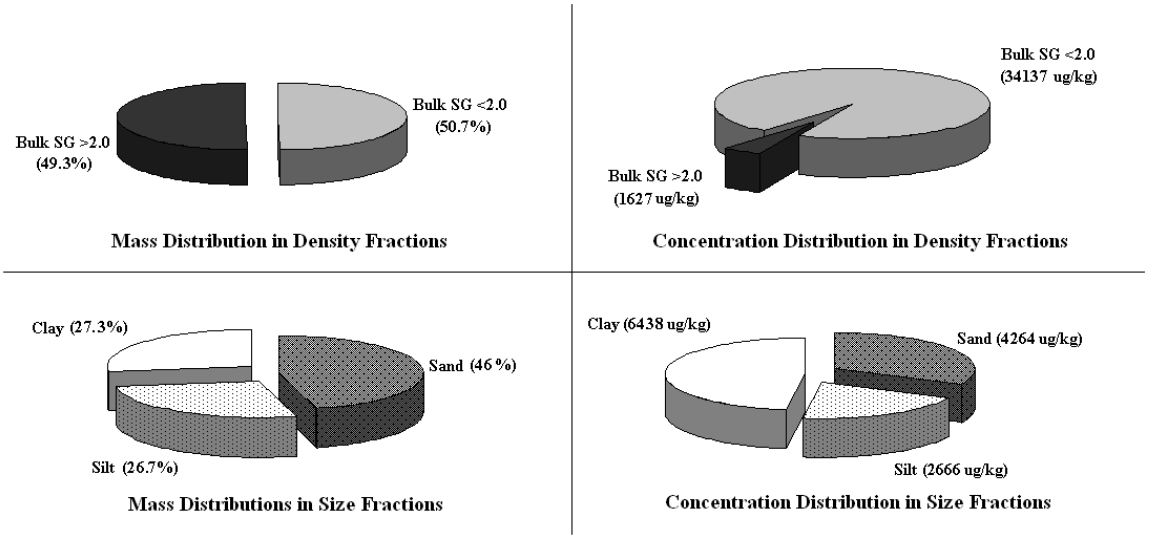


FIGURE 5-5. Calumet mean PAH mass and concentration distribution.

New Bedford. Mean PAH Concentration was nearly an order of magnitude higher in the organic fraction (13.3 percent of the sediment mass) than in the mineral fraction (Figure 5-6). On an individual basis, concentration of OG, soot, and naphthalene was comparable in the density fractions (Table 5-5). For the remainder of PAHs, concentrations were approximately two to ten times greater in the organic fraction. In the size fractions, mean PAH concentration was highest in the sand (35.1 percent of the sediment mass) and approximately equal in the silt (42.1 percent of the sediment mass) and clay (22.9 percent of the sediment mass). On an individual basis, concentration of OG was highest in the sand fraction, and approximately equal in the silt and clay. Soot was also highest in the sand fraction, although of the same order of magnitude as in the silt fraction. Soot was an order of magnitude lower in the clay. OC concentration was approximately two times greater in the clay than either the sand or the silt, however (Table 5-5). Concentration of several PAHs was nearly equal over all size fractions (with a difference of no more than 10%): benzo[b]fluoranthene, benzo[g,h,i]perylene, benzo[k]fluoranthene and Dibenzo[a,h]anthracene. With the exception of indeno[1,2,3]perylene, which was eight times higher in the sand than in the silt, the greatest concentration difference was seen for acenaphthene, which was approximately three times greater in the sand than in the clay.

On a mass basis, mean PAH mass was slightly higher in the mineral fraction (86.7 percent of the sediment mass) than in the organic fraction. In the size fractions, highest PAH mass was in the sand, followed by silt and then clay (Figure 5-6).

TABLE 5-4. Calumet Mean PAH Mass and Concentration in Size and Density Fractions

	Units		Bulk				Density Fractions								Size Fractions													
							Bulk SG <2.0			Bulk SG >2.0					Sand					Silt					Clay				
			Mass	Concentration			Mass		Conc[b]	Mass		Concentration			Mass		Concentration			Mass		Concentration			Mass		Concentration		
	Mass	Conc		Conc	SD	COV	Mass	%		Mass	%	Conc	SD	COV	Mass	%	Conc	SD	COV	Mass	%	Conc	SD	COV	Mass	%	Conc	SD	COV
Sediment Mass[a]	kg		0.636				0.039	4.3		0.866	95.7				0.350	44.2				0.309	39.1				0.132	16.7			
O&G	mg	mg/kg	2680	4215	49	0.012	1790	77.8	45900	511	22.2	590	b	b	523	43.2	1495	b	b	370	30.5	1197	b	b	319	26.3	2420	b	b
Soot	mg	mg/kg	11200	17569	2655	0.151	8010	77.9	205380	2280	22.1	2630	b	b	6650	59.5	18990	b	b	3650	32.6	11802	b	b	886	7.9	6710	b	b
OC	mg	mg/kg	56100	88217	2705	0.031	574	2.2	14720	25800	97.8	29804	b	b	21200	57.1	60474	b	b	12100	32.7	39210	b	b	3810	10.3	28870	b	b
Acenapthene	µg	µg/kg	801	1260	170	0.135	298	36.5	7640	519	63.5	599	34	0.057	554	56.5	1582	208	0.132	222	22.7	720	108	0.150	203	20.8	1540	154	0.100
Acenaphthylene	µg	µg/kg	281	442	65	0.147	98	35.9	2510	175	64.1	202	0	0.000	182	51.3	521	65	0.124	88.8	25.0	287	19	0.065	84.5	23.8	640	5	0.008
Anthracene	µg	µg/kg	2100	3305	431	0.131	975	45.7	25000	1160	54.3	1340	113	0.084	1190	45.9	3409	445	0.131	806	31.0	2608	486	0.186	603	23.2	4570	383	0.084
Benzo[a]anthracene	µg	µg/kg	3530	5550	523	0.094	2130	60.2	54500	1400	39.8	1620	198	0.122	1360	41.4	3884	930	0.239	873	26.6	2826	273	0.097	1050	32.1	7980	1412	0.177
Benzo[a]pyrene	µg	µg/kg	2780	4365	445	0.102	1610	69.3	41300	712	30.7	823	66	0.080	1240	40.9	3530	569	0.161	835	27.7	2703	152	0.056	950	31.4	7197	664	0.092
Benzo[b]fluoranthene	µg	µg/kg	2330	3655	488	0.133	1070	60.5	27500	701	39.5	810	129	0.159	869	37.6	2484	153	0.062	654	28.3	2116	139	0.066	790	34.2	5987	267	0.045
Benzo[g,h,i]perylene	µg	µg/kg	1560	2455	134	0.055	679	61.7	17400	421	38.3	486	65	0.134	758	42.1	2165	201	0.093	495	27.5	1601	199	0.125	546	30.3	4132	130	0.031
Benzo[k]fluoranthene	µg	µg/kg	1830	2875	205	0.071	605	54.7	15500	501	45.3	579	77	0.133	861	40.7	2461	252	0.102	593	28.0	1918	422	0.220	665	31.4	5037	370	0.073
Chrysene	µg	µg/kg	3290	5165	445	0.086	1720	62.5	44100	1030	37.5	1190	141	0.119	1249	41.1	3568	329	0.092	836	27.5	2704	217	0.080	954	31.4	7230	244	0.034
Dibenzo[a,h]anthracene	µg	µg/kg	403	634	114	0.180	257	64.4	6590	142	35.6	164	1	0.009	277	45.2	790	50	0.063	164	26.9	532	61	0.114	171	27.9	1294	57	0.044
Fluoranthene	µg	µg/kg	6650	10460	1047	0.100	3340	51.2	85600	3180	48.8	3670	71	0.019	2830	44.7	8070	1605	0.199	1440	22.9	4673	101	0.022	2050	32.4	15522	2418	0.156
Fluorene	µg	µg/kg	1360	2130	240	0.113	605	39.5	15500	925	60.5	1069	129	0.121	879	54.9	2510	265	0.105	456	28.5	1475	168	0.114	266	16.6	2018	1477	0.732
Indeno[1,2,3]pyrene	µg	µg/kg	1620	2550	141	0.055	913	52.8	23400	814	47.2	941	226	0.240	788	39.3	2252	323	0.143	547	27.3	1771	130	0.073	672	33.5	5094	533	0.105
2-Methylnaphthalene	µg	µg/kg	1170	1840	184	0.100	562	39.9	14400	846	60.1	977	90	0.092	1010	48.3	2895	422	0.146	619	29.5	2002	162	0.081	466	22.2	3532	155	0.044
Naphthalene	µg	µg/kg	6920	10887	141	0.013	2910	33.3	74583	5810	66.7	6713	757	0.113	6210	55.7	17749	1207	0.068	2760	24.7	8921	2432	0.273	2190	19.6	16585	4461	0.269
Phenanthrene	µg	µg/kg	6030	9475	1025	0.108	2450	44.7	62900	3040	55.3	3505	318	0.091	2960	52.1	8466	635	0.075	1440	25.4	4668	335	0.072	1280	22.5	9701	613	0.063
Pyrene	µg	µg/kg	5930	9325	1237	0.133	2410	48.4	61900	2580	51.6	2975	445	0.150	2150	44.6	6155	846	0.138	1180	24.3	3804	231	0.061	1500	31.1	11391	612	0.054
		Mean	2860	4490			Mean	50.7	34100	Mean	49.3	1630			Mean	46.0	4260			Mean	26.7	2670			Mean	27.3	6440		
All PAHs		Max	6920	10887			Max	69.3	85600	Max	66.7	6713			Max	56.5	17749			Max	31.0	8921			Max	34.2	16585		
		Min	281	442			Min	33.3	2510	Min	30.7	164			Min	37.6	521			Min	22.7	287			Min	16.6	640		
		SD	2210	3480			SD	11.3	25600	SD	11.3	1690			SD	6.1	4130			SD	2.2	2050			SD	5.6	4670		

[a] Dry fraction mass, assuming a starting mass of 1 kg wet bulk sediment. Differences in dry sediment mass for sum of density fractions, sum of size fractions and bulk sediment are due to differences in moisture content assumed in smoothed mass balance.

[b] Unreplicated data

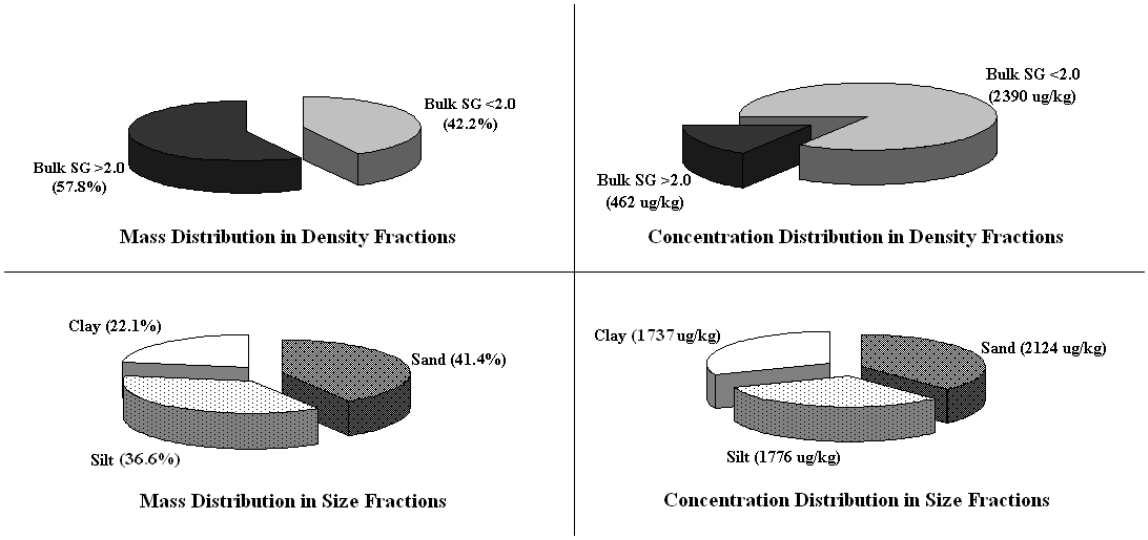


FIGURE 5-6. New Bedford mean PAH mass and concentration distribution.

New York. Mean PAH concentrations were approximately an order of magnitude higher in the organic fraction (10.6 percent of the sediment mass) than in the mineral fraction (Figure 5-7). In the size fractions, mean PAH concentration was an order of magnitude higher in the sand (23.3 percent of the sediment mass) than in the silt (22.0 percent of the sediment mass) or clay (54.7 percent of the sediment mass). Mean concentrations were also slightly higher in the silt than in the clay. On an individual basis, concentrations were three to ten times higher in the sand than in the other size fractions for all PAHs. PAH concentrations were within 20% between the silt and clay with the following exceptions: dibenzo[a,h]anthracene was 30% higher in the clay, benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[g,h,i]perylene, benzo[k]fluoranthene, chrysene and phenanthrene were all 40 to 60 percent higher in the silt than in the clay (Table 5-6).

On a mass basis, mean PAH mass was higher in the organic fraction than in the mineral fraction, despite the organic fraction comprising only 10.6 percent of the sediment mass (Figure 5-7). In the size fractions, mean PAH mass was highest in the sand fraction, followed by the clay, and then silt. On an individual basis, PAH mass was three to 10 times higher in the sand than in the silt for all compounds. Mass in the clay was more comparable to the sand, with PAH mass in sand ranging from 1.2 to 4.2 times that in the clay except for 2-methylnaphthalene which was approximately equal in the sand and clay (Table 5-6).

TABLE 5-5. New Bedford Mean PAH Mass and Concentration in Size and Density Fractions

			Bulk				Density Fractions						Size Fractions													
							Bulk SG <2.0			Bulk SG >2.0			Sand					Silt					Clay				
	Units			Concentration			Mass			Mass			Mass		Concentration			Mass		Concentration			Mass		Concentration		
	Mass	Conc	Mass	Conc	SD	COV	Mass	%	Conc[b]	Mass	%	Conc[b]	Mass	%	Conc	SD	COV	Mass	%	Conc	SD	COV	Mass	%	Conc	SD	COV
Sediment Mass[a]	kg		0.395				0.120	13.3		0.780	86.7		0.135	35.1				0.162	42.1				0.088	22.9			
O&G	mg	mg/kg	1770	4480	1032	0.230	250	14.8	2080	1440	85.2	1840	446	50.0	3300	156	0.047	276	31.0	1705	21	0.012	169	19.0	1925	191	0.099
Soot	mg	mg/kg	1170	2967	200	0.067	378	15.0	3152	2150	85.0	2752	2280	48.4	16902	b	b	2000	42.4	12350	b	b	436	9.2	4959	b	b
OC	mg	mg/kg	34400	87053	7596	0.087	6190	19.3	51568	25900	80.7	33208	3210	21.4	23798	156	0.007	5820	38.7	35945	21	0.001	5990	39.9	68116	191	0.003
Acenapthene	µg	µg/kg	68	171	6	0.033	30	50.9	253	29	49.1	38.0	43.4	57.0	321	16	0.048	23.7	31.1	146	4	0.029	9	11.9	103	4	0.035
Acenaphthylene	µg	µg/kg	12	30.0	3	0.086	5	25.8	38.0	13	74.2	17.0	5.6	36.6	41.0	2	0.048	4.7	31.2	29.0	0	0.010	5	32.3	56.0	1	0.024
Anthracene	µg	µg/kg	71	180	7	0.039	61	53.9	506	52	46.1	67.0	89.9	47.2	666	62	0.094	70.0	36.8	432	2	0.005	30	16.0	346	18	0.051
Benzo[a]anthracene	µg	µg/kg	1000	2540	28	0.011	574	47.3	4780	640	52.7	820	591	38.8	4380	71	0.016	637	41.8	3934	64	0.016	296	19.4	3368	0	0.000
Benzo[a]pyrene	µg	µg/kg	982	2485	49	0.020	353	42.6	2940	476	57.4	610	480	36.4	3555	290	0.082	569	43.1	3510	127	0.036	270	20.5	3070	0	0.000
Benzo[b]fluoranthene	µg	µg/kg	962	2435	191	0.078	426	41.9	3550	591	58.1	758	382	36.3	2833	149	0.053	435	41.4	2687	71	0.027	235	22.3	2667	127	0.048
Benzo[g,h,i]perylene	µg	µg/kg	675	1710	57	0.033	318	41.0	2650	458	59.0	587	263	34.6	1950	121	0.062	326	42.7	2010	49	0.025	173	22.7	1965	0	0.000
Benzo[k]fluoranthene	µg	µg/kg	693	1755	64	0.036	274	41.9	2280	380	58.1	487	234	33.8	1735	170	0.098	284	41.1	1755	198	0.113	174	25.1	1975	99	0.050
Chrysene	µg	µg/kg	972	2460	0	0.000	478	46.4	3980	551	53.6	706	405	37.0	3001	106	0.035	465	42.5	2870	78	0.027	225	20.5	2555	14	0.006
Dibenzo[a,h]anthracene	µg	µg/kg	148	374	5	0.013	76	40.3	636	113	59.7	145	59.8	33.2	443	47	0.106	78.2	43.4	482	3	0.006	42	23.3	477	8	0.018
Fluoranthene	µg	µg/kg	1700	4315	346	0.080	482	54.1	4020	409	45.9	524	651	37.5	4823	226	0.047	783	45.1	4833	57	0.012	301	17.3	3417	233	0.068
Fluorene	µg	µg/kg	93	235	4	0.018	47	45.5	395	57	54.5	73.0	65.0	53.3	482	8	0.016	36.9	30.3	228	25	0.112	20	16.5	229	9	0.040
Indeno[1,2,3]pyrene	µg	µg/kg	756	1915	78	0.041	670	41.5	5580	944	58.5	1210	415	57.0	3073	362	0.118	60.1	8.3	371	14	0.038	253	34.8	2877	0	0.000
2-Methylnaphthalene	µg	µg/kg	72	184	13	0.073	22	24.7	186	68	75.3	87.0	27.8	36.5	206	5	0.024	24.5	32.2	151	7	0.047	24	31.3	271	18	0.065
Naphthalene	µg	µg/kg	122	310	50	0.162	24	17.0	202	119	83.0	152	49.8	41.8	369	18	0.048	37.8	31.7	233	6	0.024	32	26.5	358	34	0.095
Phenanthrene	µg	µg/kg	284	719	21	0.030	222	59.7	1850	150	40.3	192	351	46.9	2600	57	0.022	298	39.8	1840	0	0.000	100	13.3	1135	64	0.056
Pyrene	µg	µg/kg	2050	5190	113	0.022	814	43.0	6780	1080	57.0	1380	761	39.5	5635	85	0.015	757	39.3	4673	341	0.073	410	21.3	4658	49	0.011
		Mean	627	1590			Mean	42.2	2390	Mean	57.8	462	Mean	41.4	2120			Mean	36.6	1780			Mean	22.1	1740		
All PAHs		Max	2050	5190			Max	59.7	6780	Max	83.0	1380	Max	57.0	5635			Max	45.1	4833			Max	34.8	4658		
		Min	12	30			Min	17.0	38	Min	40.3	17	Min	33.2	41			Min	8.3	29			Min	11.9	56		
		SD	607	1540			SD	11.0	2130	SD	11.0	419	SD	7.9	1790			SD	8.9	1700			SD	6.4	1470		

[a] Dry fraction mass, assuming a starting mass of 1 kg wet bulk sediment. Differences in dry sediment mass for sum of density fractions, sum of size fractions and bulk sediment are due to differences in moisture content assumed in smoothed mass balance.

[b] Unreplicated data

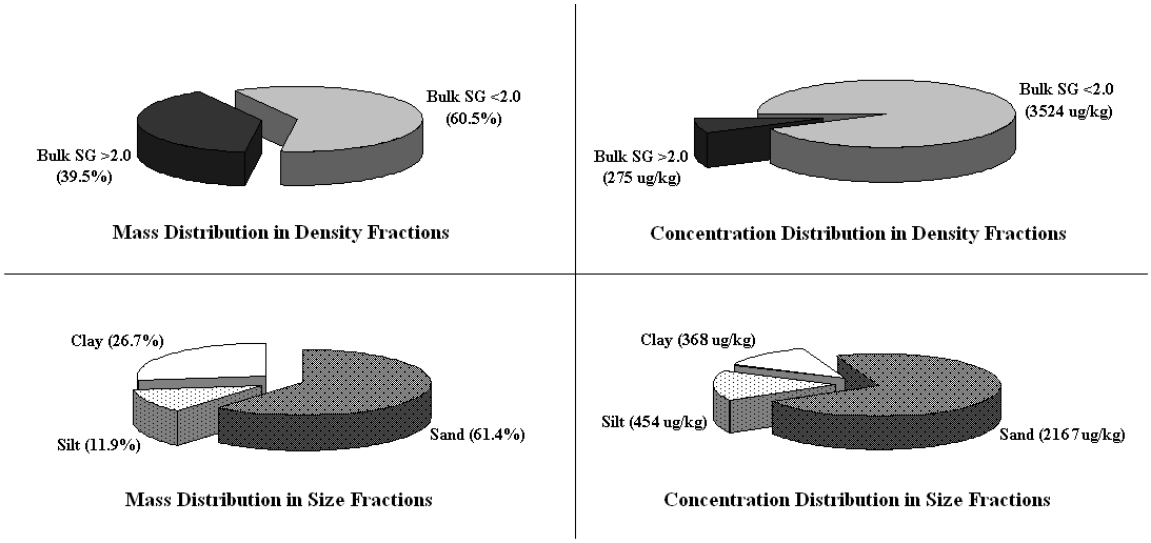


FIGURE 5-7. New York mean PAH mass and concentration distribution.

DISCUSSION

Large concentration differences were seen for PAHs between organic and mineral fractions for all three sediments, with concentrations one to two orders of magnitude greater in the organic fraction. While clay also appears to play a role in PAH sorption for these sediments, organic sorption appears to dominate over sorption to clay. Clay and organic fraction concentrations were most comparable for the New Bedford sediment. For New York, mean concentrations in the organic fraction were an order of magnitude higher than in the clay fraction. In Calumet, mean organic fraction concentrations were about five times greater than in the clay. Because the clay size fraction contains both mineral and organic components, however, the role of clay minerals with respect to the contaminant loading in this fraction is difficult to isolate and quantify without statistical analysis. The presence of contaminants in the clay fraction is not a definitive indication of sorption to the clay minerals. In fact, there are components of all the sorptive phases in each of the size and density fractions. This may be attributable to either the range of physical properties of each of these phases, or inefficiency of the separations, or both.

Contaminant distribution was variable for the size fractions, with highest concentrations typically found in either the sand or the clay, with a few exceptions. Corresponding distribution of sorptive phases was also variable. In several cases, concentration of sorptive phases was very high in a given fraction, but the mass was comparable to or lower than that in the other fractions due to the mass distribution of the sediment fractions. OG and soot concentrations were higher in the organic fraction than in the mineral fraction for all three sediments. OC concentration was higher in the mineral phase for Calumet, and was two orders of magnitude higher on a mass basis. Concentration of OC was higher in the organic fraction for New Bedford and New York, but mass of OC was an order of magnitude higher in the mineral fraction for New Bedford, and was the same order of magnitude in New York. Given the variability of phase concentrations between the fractions, and the influence of the relative mass distribution, correspondence of contaminant distribution to the sorptive phases is not clear-cut. Correlations between PAHs, OG, soot and OC will be explored using statistical techniques in Chapter 7. Some general

TABLE 5-6. New York Mean PAH Mass and Concentration in Size and Density Fractions

	Units		Bulk				Density Fractions						Size Fractions													
							Bulk SG <2.0			Bulk SG >2.0			Sand					Silt					Clay				
			Mass	Concentration			Mass		Conc[b]	Mass		Conc[b]	Mass		Concentration			Mass		Concentration			Mass		Concentration		
	Mass	Conc		Conc	SD	COV	Mass	%		Mass	%		Mass	%	Conc	SD	COV	Mass	%	Conc	SD	COV	Mass	%	Conc	SD	COV
Sediment Mass[a]	kg		0.367				0.038	10.6		0.322	89.4		0.057	23.3				0.054	22.0				0.134	54.7			
O&G	mg	mg/kg	1206	3285	2383	0.725	201	71.8	5290	79	28.2	245	209	66.3	3660	198	0.054	27	8.7	509	93	0.182	79	25.0	588	29	0.049
Soot	mg	mg/kg	3540	9648	8960	0.929	175	30.0	4613	409	70.0	1269	572	41.6	10043	b	b	259	18.8	4792	b	b	546	39.6	4072	b	b
OC	mg	mg/kg	18800	51317	383	0.007	2770	30.1	72897	6440	69.9	19986	1500	29.4	26297	198	0.008	470	9.2	8699	93	0.011	3130	61.4	23340	29	0.001
Acenapthene	µg	µg/kg	20	55.0	8	0.154	15	59.4	396	10	40.6	32.0	18	75.1	321	161	0.501	2	7.2	32.0	1	0.018	4	17.8	32.0	10	0.318
Acenaphthylene	µg	µg/kg	8	22.0	8	0.381	4	64.1	118	3	35.9	<10.0	5	67.3	90.0	64	0.709	1	7.9	11.0	1	0.130	2	24.8	14.0	4	0.305
Anthracene	µg	µg/kg	175	477	31	0.065	76	63.2	2010	44	36.8	138	57	62.2	1007	429	0.426	9	10.2	175	13	0.077	25	27.6	190	61	0.320
Benzo[a]anthracene	µg	µg/kg	284	775	95	0.123	242	67.7	6380	116	32.3	359	177	68.9	3101	594	0.192	31	12.2	579	35	0.060	49	18.9	362	122	0.336
Benzo[a]pyrene	µg	µg/kg	307	837	99	0.118	229	67.0	6020	113	33.0	350	197	66.8	3450	198	0.057	39	13.1	713	47	0.065	59	20.2	444	115	0.260
Benzo[b]fluoranthene	µg	µg/kg	285	777	49	0.063	166	61.6	4370	103	38.4	321	161	62.3	2830	226	0.080	37	14.2	683	50	0.072	61	23.5	454	139	0.307
Benzo[g,h,i]perylene	µg	µg/kg	204	557	50	0.090	109	60.2	2870	72	39.8	224	122	63.3	2140	42	0.020	27	13.9	497	47	0.094	44	22.7	327	72	0.221
Benzo[k]fluoranthene	µg	µg/kg	205	558	14	0.025	109	58.7	2870	77	41.3	238	147	62.0	2570	198	0.077	32	13.6	594	2	0.004	58	24.4	431	122	0.284
Chrysene	µg	µg/kg	299	815	85	0.104	211	66.0	5560	109	34.0	338	212	67.4	3716	375	0.101	39	12.5	726	44	0.060	63	20.1	471	155	0.329
Dibenzo[a,h]anthracene	µg	µg/kg	46	124	8	0.068	27	46.4	712	31	53.6	97.0	26	50.4	458	24	0.052	6	11.2	107	11	0.106	20	38.4	149	127	0.854
Fluoranthene	µg	µg/kg	514	1400	28	0.020	358	62.4	9410	215	37.6	668	311	63.1	5461	184	0.034	59	11.9	1089	129	0.119	123	25.0	918	342	0.373
Fluorene	µg	µg/kg	30	81.0	7	0.084	24	64.3	637	13	35.7	42.0	17	58.0	301	137	0.456	3	11.4	62.0	3	0.053	9	30.6	68.0	24	0.352
Indeno[1,2,3]pyrene	µg	µg/kg	213	582	45	0.077	144	51.0	3780	138	49.0	428	115	58.5	2020	99	0.049	27	13.6	497	42	0.084	55	27.9	410	207	0.504
2-Methylnaphthalene	µg	µg/kg	55	150	23	0.156	24	57.6	631	18	42.4	55.0	19	44.3	336	103	0.307	6	13.3	107	5	0.046	18	42.5	137	83	0.608
Naphthalene	µg	µg/kg	81	221	59	0.269	35	60.8	931	23	39.2	71.0	27	48.1	480	158	0.329	7	12.8	135	17	0.126	22	39.0	166	79	0.474
Phenanthrene	µg	µg/kg	732	1995	7	0.004	162	67.6	4270	78	32.4	242	140	69.3	2455	1252	0.510	23	11.3	422	37	0.089	39	19.5	294	84	0.287
Pyrene	µg	µg/kg	732	1995	219	0.110	340	49.9	8950	341	50.1	1060	348	57.5	6107	531	0.087	70	11.6	1295	35	0.027	187	30.9	1395	531	0.380
All PAHs		Mean	246	672			Mean	60.5	3520	Mean	39.5	275	Mean	61.4	2170			Mean	11.9	454			Mean	26.7	368		
		Max	732	1995			Max	67.7	9410	Max	53.6	1060	Max	75.1	6107			Max	14.2	1295			Max	42.5	1395		
		Min	8	22			Min	46.4	118	Min	32.3	8	Min	44.3	90			Min	7.2	11			Min	17.8	14		
		SD	227	618			SD	6.30	2960	SD	6.30	267	SD	8.10	1830			SD	2.0	379			SD	7.5	344		

[a] Dry fraction mass, assuming a starting mass of 1 kg wet bulk sediment. Differences in dry sediment mass for sum of density fractions, sum of size fractions and bulk sediment are due to differences in moisture content assumed in smoothed mass balance.

[b] Unreplicated data

relationships can be derived based on the results of the fractionation study, however, which are of utility in assessing feasibility of contaminant reduction by size or density separation.

Final contaminant concentration resulting from removal of a selected size or density fraction can be expressed as:

$$C_F = C_I * \left(\frac{1 - f_i}{1 - f_{sed}} \right) \tag{5-11}$$

where

f_i = fraction contaminant mass removed
f_{sed} = fraction of sediment mass removed
C_I = contaminant concentration in bulk sediment, µg/kg
C_F = contaminant concentration in treated sediment, µg/kg

The percent reduction (R) in contaminant concentration is given by

$$R = \left(1 - \left(\frac{1 - f_i}{1 - f_{sed}} \right) \right) * 100 \tag{5-12}$$

A summary of the contaminant reduction resulting from removal of operationally defined clay and organic fractions for the three sediments studied is given in Table 5-7. Negative values indicate that higher concentrations would be expected in the treated sediment than in the untreated sediment. If the proportionality in Equation 5-13 is greater than 1, higher concentrations will result in the residuals. For Calumet, there was only one instance where higher concentrations were predicted in the treated sediment for removal of the clay fraction. Highest mean reduction of PAHs resulted from removal of the organic fraction. For New Bedford, removal of the clay resulted in higher contaminant concentration for all but five PAHs in the treated materials, while removal of the organic fraction resulted in contaminant reduction for all. For New York, removal of the clay fraction resulted in higher concentration in the remaining materials for all PAHs. Removal of the organic fraction resulted in positive reduction for all PAHs.

Table 5-7. Percent Reduction in PAH Concentration (R) with Removal of Selected Operationally Defined Fractions

	Clay Fraction Removed			Organic Fraction Removed		
Sediment	**Min[a]**	**Max[a]**	**Mean[b]**	**Min[a]**	**Max[a]**	**Mean[b]**
Calumet	-.05	20.9	12.8	30.3	68.0	48.4
New Bedford	-14.3	15.4	-1.0	4.2	53.5	33.3
New York	-81.5	-27	-61.8	40.1	63.9	55.8

[a] Minimum or maximum percent removal for an individual compound
[b] Mean percent removal for all PAHs

SUMMARY AND CONCLUSIONS

Achieving reduction of contaminant concentrations by selective separation of a highly contaminated fraction is dependent upon a favorable contaminant to sediment mass ratio in the fraction removed. If the sediment mass of the targeted fraction is large relative to the concentration in that fraction, concentration in the remaining materials may be higher after removal of this fraction, rather than lower. This illustrates the importance of fractionation data to feasibility analysis for separation. The proportion and character of materials reporting to the process streams can be assessed and sediment and contaminant mass balance constructed for preliminary treatability evaluations. An appropriate target fraction can be identified, and the processes and equipment selected based on the specific requirements for effective separation of that fraction from the bulk sediment. Determination of phase specific contaminant levels would be even more helpful in that processes could be tailored to removal of a specific phase, rather than a specific sediment fraction, and incremental contaminant reduction expected as a result could be estimated with simple mass balance procedures such as those developed here.

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CHAPTER 6

FRACTIONATION STUDY OF NATURAL SEDIMENTS FOR DETERMINING PAH AND PCB DISTRIBUTION – PART 2: PCBS

INTRODUCTION

The fate of contaminants mobilized from sediment during dredging and disposal is of concern in Section 404 (Clean Water Act) evaluations (USEPA/USACE 2004). To demonstrate compliance with water quality standards and assess the need for mixing zones or mitigation measures, the magnitude of contaminant release resulting from a dredging action is evaluated for applicable contaminant exposure pathways (USEPA/USACE 1991, 1998; USACE 2003). Additionally, because disposal space for dredged material is becoming more limited in some areas of the United States, alternative management practices are increasingly being considered (Great Lakes Commission 2004; Price et al. 1997). Separation of relatively clean fractions of the sediment for beneficial use reduces the amount of dredged material requiring confined disposal (Olin-Estes and Palermo 2001).

In both cases, contaminant partitioning and distribution are central to alternatives analysis (USEPA/USACE 1991, 1998; USACE 2003). Effluent quality, for example, is based upon evaluation of contaminant solubility under two boundary conditions: 1) mixing of sediment pore water and the overlying carrier water, and 2) equilibrium between sediment, pore water and carrier water. Equilibrium calculations require knowledge of the partitioning behavior of the contaminants of concern. Theoretical partitioning coefficients may be developed based on site specific sediment and contaminant properties (Hansen et al. 1999; Brannon et al. 1998; Chiou, McGroddy and Kile 1998; DiToro et al. 1991; Pardue et al. 1993), values may be obtained from published references, or an observed coefficient may be calculated from sediment and pore water data (EPA 1999). Disparity of theoretical and observed partitioning coefficients may be as much as an order of magnitude or more, however (Kan et al. 1998). These differences are usually resolved and representative values selected by taking into account other available information, such as the results of an elutriate test (Palermo 1986). Alternatively, the most conservative values are selected for the analysis. Fractionation studies may be also conducted to evaluate the association of contaminants with specific size or density fractions of sediments, to assess the feasibility of separation for contaminant reduction or to assess the suitability of material for beneficial use (Olin-Estes and Palermo 2001; Olin et al. 1999).

PCBs are hydrophobic organic compounds commonly found in sediments of navigation waterways (National Research Council 1997; USEPA 1993). PCBs are chlorinated, aromatic compounds that were produced for use as dielectric fluids in capacitors and transformers and as industrial fluids in various systems (Hutzinger et al. 1983). There are 209 congeners, of which approximately 150 congeners are found in the environment (Hansen et al. 1999). PCBs are highly lipophilic with low solubility in water, with solubility decreasing with increasing degree of chlorination. PCBs of higher molecular weight tend to be associated with mineral and organic particulates in the environment, with organic sorption dominating (Girvin and Scott 1997; Karichoff 1984). The presence of high levels of dissolved organic carbon may increase the apparent solubility of PCBs (Brannon et al. 1998; Hwang et al. 1998), although aromaticity of

the DOC may be important, as was shown for PAHs, which have lower affinity for aliphatic (non-aromatic) carbon (Hwang and Cutright 2004).

The major objectives of this research effort were to ascertain the distribution trends of PCBs in three natural sediments and to evaluate the potential usefulness of fractionation studies to treatability and fate and effects evaluations. Fractionation studies offer a vehicle to evaluate the association of contaminants with specific phases of sediments and to establish correlations to those phases from which more global partitioning coefficients might be derived. This research effort was developed to meet the dual objectives of developing simple bench scale testing methods for separation feasibility evaluations and laying a foundation for improved understanding of the target phases important to contaminant reduction.

MATERIALS AND METHODS

Sediments and Analytes. Materials employed in the separation study included one freshwater and two marine sediments. The freshwater sediment was obtained at the offloading point to the confined disposal facility (CDF) for Calumet River. The marine sediments were taken directly from the harbor in New York and New Bedford. Sediments were packaged in 5-gallon HDPE buckets and maintained at 4°C during transport and while in storage.

Sediments were homogenized in a large stainless steel mixer when received at the laboratory. Aliquots of homogenized sediment were tested to determine specific gravity of solids (MD0302), moisture content, grain size distribution (ASTM D422), classification (ASTM D2488), fraction organic carbon (ASTM D2974), cation exchange capacity (CEC) (SW-846 Method 9080/9081), pH (SW-846 Method 9040B), and fraction expandable clay (x-ray diffraction). Soot analysis was conducted using the procedure reported in Gustafsson et al. (1997), which is essentially a modification of the acidification and combustion procedure used for TOC determination (SW-846 9060). Samples were also analyzed in duplicate for selected analytes, using SW-846 methods. These samples were packaged in amber glass jars with Teflon® lids and maintained at 4ºC without preservatives, prior to analysis. Samples were analyzed for 70 different PCB congeners. Congeners representative of each homolog group, found in common aroclors, and that typically can be resolved without co-elution, were selected. Sediments were also analyzed for oil and grease (O&G), and total organic carbon (TOC).

Samples of pore water were obtained by centrifuging homogenized sediment. Pore water was analyzed for the same constituents as the sediments, as well as dissolved organic carbon (DOC). Due to volume limitations, only PCBs were analyzed in duplicate in the pore water.

Density Separations. A solution of non-toxic, water-soluble sodium polytungstate was used for the density separations. The heavy media was made up to give a solution density of 2.0 g/cm^3 when mixed with the sediment, adjusting for expected dilution from pore water in the sediment sample. In order to prevent formation of a calcium precipitate in the media, calcium ions were removed from the sediment by saturating the sediment with a 1N Sodium Acetate solution at a 6:1 water:sediment ratio. This was tumbled overnight and centrifuged, and supernatant decanted. The procedure was repeated once with sodium acetate and again with distilled, de-ionized water (DDI) to remove the sodium acetate.

Samples of pretreated bulk sediment were placed in 250-ml Nalgene® centrifuge bottles with the solution of sodium polytungstate. Samples were sonicated briefly in a water bath to encourage separation of the different density materials and then centrifuged until a clear

separation of phases occurred. The light (organic) fraction was decanted onto a microfiltration apparatus and rinsed with DDI water to remove residual heavy media. Initially, filters used were Whatman GF/F Glass Microfibre Filters (0.7-µm). Because solids were difficult to remove from these filters, Lida 0.45-µm nylon filter membranes were later substituted. Filtration through the nylon filters was slower, but removal of solids from the filters was less problematic. The heavy (mineral) fraction was recombined with additional sodium polytungstate and the procedure repeated until no further organic phase could be separated from the mineral phase. The heavy fraction was then recombined with DDI water, sonicated, centrifuged and decanted through a microfiltration apparatus to remove residual heavy media. Samples from each density fraction were analyzed on the Coulter LS 100 particle size analyzer (Beckman Coulter, Inc., USA) to determine particle size distribution.

The density separation was performed once per sediment. Wet solids were collected from the microfiltration apparatus and placed in amber glass jars with Teflon-lined lids for chemical and physical analysis. No preservatives were added. Samples were maintained in storage at 4°C. Replicate samples were obtained from the mineral fraction where sufficient material was available. Material volume was insufficient for replicates from the organic fraction.

Size Separations. Size separation of homogenized sediment was accomplished in three stages. A specified amount of wet sediment, sufficient to produce adequate quantities of each fraction, was weighed out and wet sieved through a 4.75-mm sieve and a 200-mesh (75-µm) sieve. Material retained on the coarse sieve was classified as oversize and was not tested. Material retained on the fine sieve was classified as sand. Slurry passing the 200-mesh sieve was diluted to approximately 15 percent solids by weight and processed through a 2-inch Mozely hydrocyclone. Underflow was designated as the operationally defined silt fraction; overflow was designated as the operationally defined clay fraction. Both silt and clay fractions were dewatered using a continuous flow CF 35M Microseparator. Samples from each size fraction were analyzed on the Coulter Counter to evaluate particle size distribution.

The size separation was performed only once for each sediment; however, where sufficient quantities of material were available, replicate samples of each operational size fraction were taken for chemical and size distribution analysis. Wet solids were placed in amber glass jars with Teflon-lined lids for chemical and physical analysis. No preservatives were added. Samples were maintained at 4°C.

RESULTS

Physical Characterization. Physical properties of the three sediments and results of the x-ray diffraction analysis are summarized in Chapter 5, Table 5-1. A short synopsis is provided here. All three sediments are classified as sandy silt (ML). Calumet is the coarsest sediment, with a comparatively low organic fraction, and a trace of gravel. New Bedford contains the highest proportion of organic materials, followed by New York. New York is the finest sediment with the highest proportion of clay. Smectite and mixed layer clays were present in all three sediments. Cation exchange capacity was comparable for the three sediments.

Chemical Characterization. Results of the chemical characterization of the bulk sediments and pore water are also summarized in Chapter 5, Table 5-2. Sediment and pore water PCB concentrations reported represent there are the mean of two replicates, with the exception of

TOC, DOC and O&G in the pore water which were not replicated due to limited pore water volume. Data in Table 5-2 is raw data.

Mass Balance. Recovery of all solids for gravimetric mass balance was not feasible due to processing losses and slurry volumes generated in the cyclone separation. The relative distribution of sediment mass to each size and density fraction was estimated based on measured properties of the bulk sediment and the resulting fractions. The procedure was described in Chapter 5, Equations 5-1 through 5-10. Mass of sediment reporting to each fraction is illustrated in Figure 5-1.

Distribution of Sorptive Phases. The distribution of OG, soot and OC in the study sediments is summarized in Chapter 5 and illustrated in Figures 5-2 through 5-4. The mass of organic carbon was much larger than either OG or soot (ranging from 1.4 to 82 times as much) in all fractions for all sediments except the organic fraction of Calumet. Here, the mass of soot was found to be approximately 14 times greater than OC. The relative distribution of the phases between the size and density fractions was distinctly different for each sediment, as can be seen by examining Figures 5-2 through 5-4.

PCB DISTRIBUTION

Calumet. Mean PCB concentration was approximately an order of magnitude higher in the organic fraction (4.3 percent of the sediment mass) than in the mineral fraction (Figure 6-1). In the size fractions, mean PCB concentration in the clay (16.7 percent of the sediment mass) was approximately two times the concentrations in the sand (44.2 percent of the sediment mass), and three times concentrations in the silt (39.1 percent of the sediment mass). This was true on an individual congener basis as well, with concentration in the clay ranging from approximately 1.5 to 9 times the concentrations in the silt and sand fractions (Table 6-1).

On a mass basis, mean PCB mass was highest in the mineral fraction, which comprises 95.7 percent of the sediment mass (Figure 6-1). On an individual basis, PCB mass was also highest in the mineral fraction, except for PCB 54 (30.6 percent) and PCB 206 (49.7 percent). In the size fractions, mean PCB mass was approximately equal in the sand and clay fractions. On an individual basis, highest PCB mass was found in the sand for 28 PCBs and in the clay for the remaining 10 PCBs. PCB mass in silt was about 70-80 percent of the mass in sand and clay fractions individually. Mean PCB mass in clay was 95 percent of mass in sand (Table 6-1).

New Bedford. Mean PCB concentration in the organic fraction (13.3 percent of the sediment mass) was approximately two times the concentration in the mineral fraction (Figure 6-2). Concentrations between the density fractions differed by as much as an order of magnitude for some congeners, but were always higher in the organic fraction (Table 6-2). In the size fractions, mean PCB concentration in the clay (22.9 percent of the sediment mass) was approximately two times the mean concentration in the sand (35.1 percent of the sediment mass) and approximately 4 times higher than the mean concentration in the silt (42.1 percent of the sediment mass).

On a mass basis, 76.9 percent of the PCBs were in the mineral fraction, which comprises 86.7 percent of the sediment mass (Figure 6-2). This distribution was also relatively consistent for individual congeners in the density fractions. In the size fractions, mean PCB mass was

approximately equal in the sand and clay fractions (37.4 percent and 41.2 percent of total PCB mass respectively). Mean PCB mass in the silt was 21.4 percent, and ranged from 14.9 to 29.9 percent for the individual congeners. On an individual congener basis, highest PCB mass was found consistently in the sand for 15 congeners and in the clay for the remaining 30 congeners (Table 6-2).

New York. Mean PCB concentration in the organic fraction (10.8 percent of the sediment mass) was approximately two times the concentration in the mineral fraction (Figure 6-3). Concentrations of individual congeners were as much as an order of magnitude higher in the organic fraction than the mineral fraction, except for PCBs 8, 18, 49 and 52, which were higher in the mineral fraction. Mean PCB concentrations in sand (23.3 percent of sediment mass) were slightly higher than in the clay (54.6 percent of sediment mass) and approximately two times the concentration in the silt (22.1 percent of sediment mass). Concentration of individual congeners in sand ranged from 0.1 to 9 times that of clay concentrations, and 0.8 to 7 times that of silt concentrations. Concentration of PCBs 7, 8, 18, 28, 44, 49, and 52 were highest in the clay (Table 6-3). Composite PCB concentration for the size fractions (Figure 6-3) does not fall within the same range as the composite concentration for the density fractions. This is attributed to greater sample variability for this sediment, and the influence of one outlier in the density fraction data.

On a mass basis, 67.8 percent of the PCBs were in the mineral fraction, which comprises 89.2% of the sediment mass (Figure 6-3). Mass distribution of individual congeners in the mineral fraction varied widely from 0 to effectively 100 percent. Mass of PCBs 189 and 206 were slightly higher in the organic fraction. PCB 208 was found only in the organic fraction. In the size fractions, mass distribution of individual congeners varied widely, ranging from 18 to 91.6 percent in the clay, 5 to 71.1 percent in the sand, and 3.3 to 20.2 percent in the silt (Table 6-3).

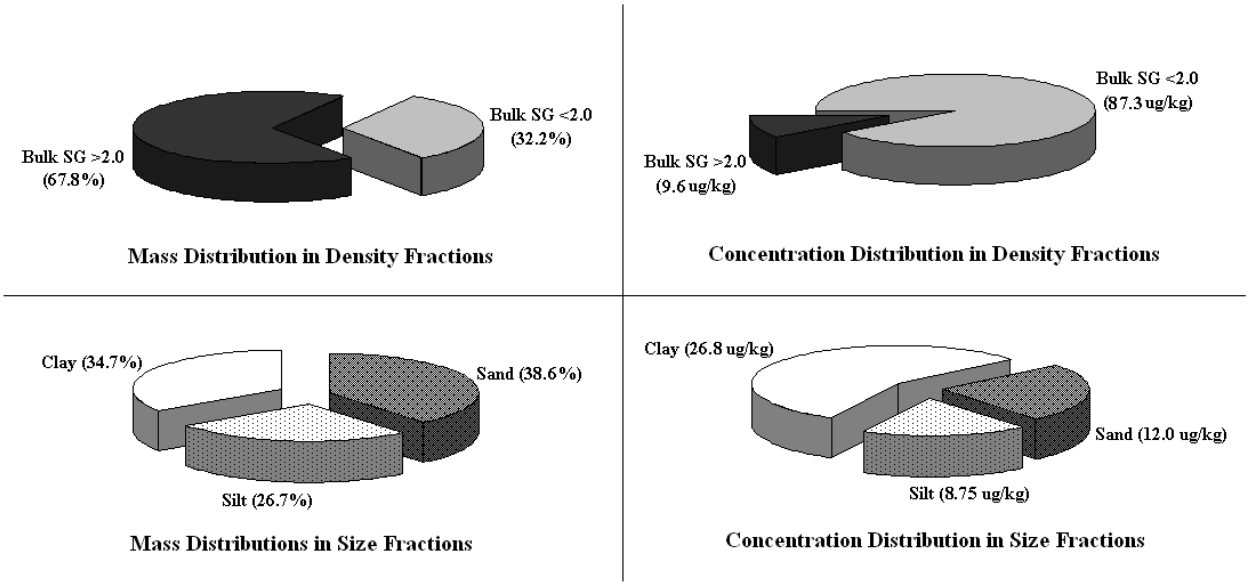

FIGURE 6-1. Calumet mean PCB mass and concentration distribution.

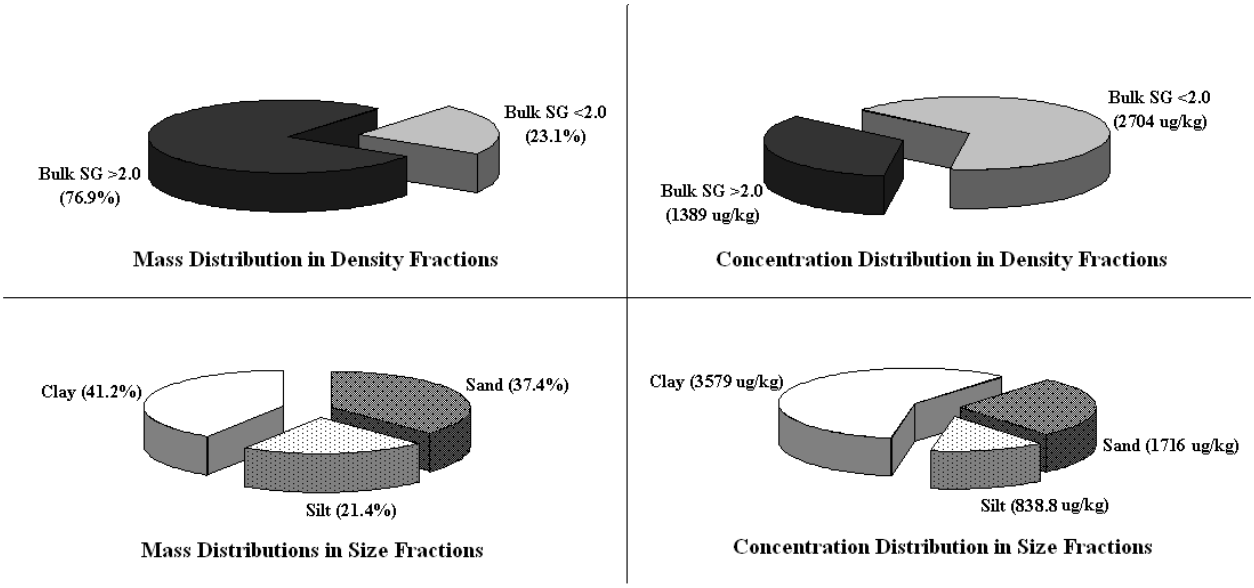

FIGURE 6-2. New Bedford mean PCB mass and concentration distribution.

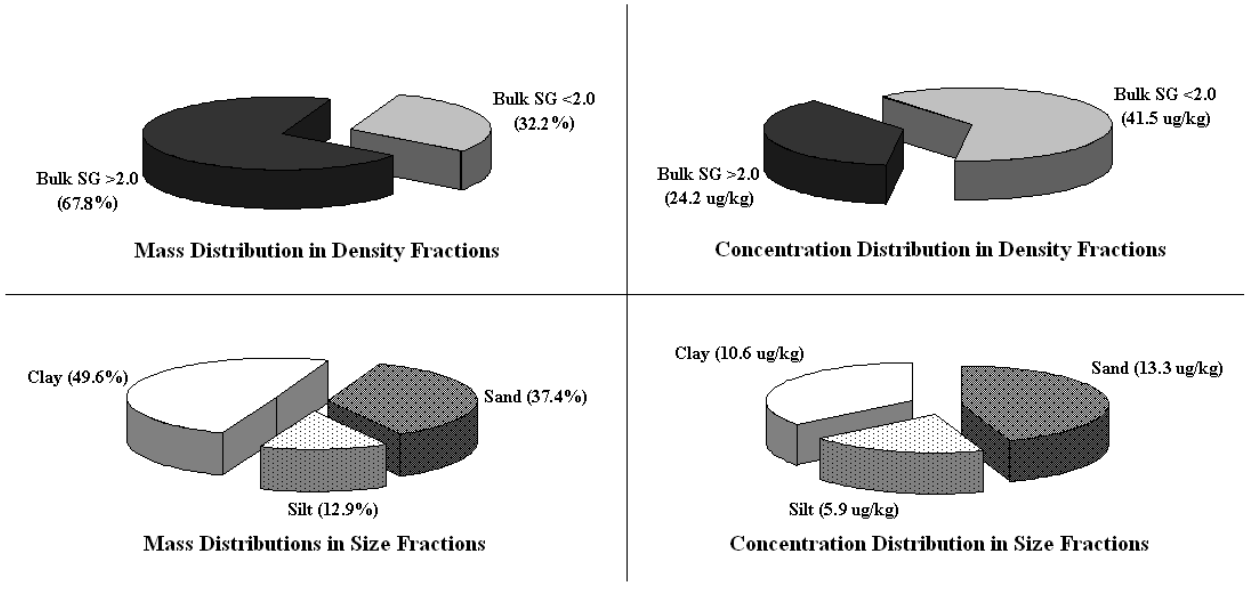

FIGURE 6-3. New York mean PCB mass and concentration distribution in fractions.

TABLE 6-1. Calumet Mean PCB Mass and Concentration in Size and Density Fractions

	Units		Bulk				Density Fractions: Bulk SG<2			Density Fractions: Bulk SG>2			Size Fractions: Sand					Size Fractions: Silt					Size Fractions: Clay				
	Mass	Conc	Mass	Concentration			Mass			Mass			Mass		Concentration			Mass		Concentration			Mass		Concentration		
				Conc	SD	COV	Mass	%	Conc[b]	Mass	%	Conc[b]	Mass	%	Conc	SD	COV	Mass	%	Conc	SD	COV	Mass	%	Conc	SD	COV
Sediment Mass[a]	kg		0.667				0.039	4.30		0.866	95.7		0.350	44.2				0.309	39.1				0.132	16.7			
PCB101	µg	µg/kg	40.6	60.8	0.04	0.001	9.83	34.3	252	18.8	65.7	21.7	8.56	35.0	24.5	7.00	0.29	6.57	26.9	21.3	3.46	0.163	9.33	38.1	70.7	16.5	0.233
PCB114	µg	µg/kg		<5.15					<10.6	1.46	81.9	1.69	0.51	39.9	1.47	0.29	0.20	0.36	28.0	1.17	0.15	0.131	0.41	32.1	3.13	0.31	0.098
PCB118	µg	µg/kg	30.7	46.0	1.27	0.028	6.71	30.7	172	15.2	69.3	17.5	6.20	35.1	17.7	5.63	0.32	5.36	30.3	17.3	1.70	0.098	6.12	34.6	46.4	1.75	0.038
PCB128	µg	µg/kg	6.00	9.00	0.40	0.045	1.21	34.7	31.1	2.28	65.3	2.63	1.02	33.7	2.90	0.44	0.15	0.89	29.4	2.87	0.25	0.088	1.11	36.8	8.40	0.44	0.052
PCB136	µg	µg/kg	3.64	5.45	3.21	0.589			<10.6	3.57	94.5	4.12	0.98	34.4	2.80	1.65	0.59	0.61	21.4	1.97	0.45	0.229	1.26	44.2	9.53	3.27	0.343
PCB137	µg	µg/kg					0.53	32.0	13.7	1.13	68.0	1.31	0.44	35.4	1.25	0.28	0.22	0.36	29.5	1.18	0.02	0.015	0.43	35.1	3.28	0.16	0.048
PCB138	µg	µg/kg	26.8	40.2	0.07	0.002	5.62	31.4	144	12.3	68.6	14.2	4.69	33.4	13.4	2.69	0.20	4.13	29.5	13.4	1.21	0.090	5.20	37.1	39.4	1.65	0.042
PCB141	µg	µg/kg	5.85	8.78	1.01	0.115	1.03	25.5	26.4	3.01	74.5	3.47	1.09	38.9	3.10	1.31	0.42	0.76	27.3	2.47	0.06	0.023	0.94	33.8	7.13	0.38	0.053
PCB151	µg	µg/kg	6.88	10.3	2.52	0.245	1.66	35.9	42.6	2.96	64.1	3.42	1.39	40.0	3.97	0.90	0.23	0.99	28.5	3.20	0.35	0.108	1.09	31.5	8.27	0.57	0.069
PCB156	µg	µg/kg		<5.15	0.09	0.021			<10.6	1.03	73.7	1.19	0.68	39.5	1.93	0.92	0.48	0.50	29.4	1.63	0.12	0.071	0.53	31.1	4.03	0.15	0.038
PCB170	µg	µg/kg		<5.15			0.94	39.2	24.2	1.46	60.8	1.69	0.75	35.3	2.13	0.32	0.15	0.59	27.8	1.90	0.36	0.190	0.78	36.9	5.90	0.72	0.122
PCB 18	µg	µg/kg	57.8	86.6	4.24	0.049	10.0	26.8	257	27.4	73.2	31.6	17.7	44.6	50.6	24.7	0.49	9.35	23.6	30.3	3.89	0.129	12.6	31.8	95.4	24.7	0.259
PCB180	µg	µg/kg	5.21	7.81	0.73	0.093	1.46	38.2	37.4	2.36	61.8	2.73	1.67	43.2	4.77	1.42	0.30	1.01	26.1	3.27	0.49	0.151	1.18	30.7	8.97	0.32	0.036
PCB183	µg	µg/kg		<5.15	0.25	0.130	0.50	41.0	12.8	0.72	59.0	0.83	0.41	37.1	1.17	0.31	0.26	0.29	26.2	0.93	0.06	0.062	0.40	36.7	3.07	0.21	0.068
PCB189	µg	µg/kg		<5.15					<10.6			<0.46			<0.47					<0.45					<0.69		
PCB194	µg	µg/kg		<5.15	0.11	0.063	0.31	29.4	<10.6	0.74	70.6	0.86	0.40	41.7	1.13	0.25	0.22	0.28	29.2	0.90	0.10	0.111	0.28	29.1	2.10	0.20	0.095
PCB195	µg	µg/kg		<5.15					<10.6			<0.46			<0.47					<0.45			0.10	35.2	0.73	0.06	0.079
PCB196	µg	µg/kg		<5.15					<10.6						<0.47					<0.45			0.18	39.7	1.37	0.06	0.042
PCB199	µg	µg/kg		<5.15					<10.6			<0.46			<0.47					<0.45					<0.69		
PCB201	µg	µg/kg		<5.15			0.42	31.5	10.7	0.91	68.5	1.05	0.44	43.4	1.27	0.06	0.05	0.28	27.2	0.90	0.17	0.192	0.30	29.3	2.27	0.23	0.102
PCB203	µg	µg/kg		<5.15			0.47	32.0	12.1	1.00	68.0	1.16	0.26	41.1	0.73	0.15	0.21	0.16	26.4	0.53	0.15	0.286	0.20	32.4	1.53	0.49	0.322
PCB206	µg	µg/kg		<5.15					<10.6			<0.46	0.27	40.3	0.77	0.15	0.20	0.22	32.5	0.70	0.17	0.247	0.18	27.1	1.37	0.06	0.042
PCB208	µg	µg/kg		<5.15											<0.47					<0.45			0.10	33.1	0.75	0.07	0.094
PCB 28	µg	µg/kg	62.5	93.8	5.59	0.060	12.8	25.8	327	36.6	74.2	42.3	16.8	33.6	47.9	21.4	0.45	13.52	27.1	43.8	1.80	0.041	19.6	39.2	148.1	4.97	0.034

(continued)

TABLE 6-1. (Continued)

	Units		Bulk				Density Fractions: Bulk SG<2			Density Fractions: Bulk SG>2			Size Fractions: Sand					Size Fractions: Silt					Size Fractions: Clay				
	Mass	Conc	Mass	Concentration			Mass			Mass			Mass		Concentration			Mass		Concentration			Mass		Concentration		
				Conc	SD	COV	Mass	%	Conc[b]	Mass	%	Conc[b]	Mass	%	Conc	SD	COV	Mass	%	Conc	SD	COV	Mass	%	Conc	SD	COV
PCB 40	µg	µg/kg	16.7	25.1	17.5	0.697	1.93	29.6	49.6	4.60	70.4	5.31	2.78	42.1	7.95	3.75	0.47	1.62	24.5	5.25	0.21	0.040	2.21	33.4	16.8	1.63	0.097
PCB 44	µg	µg/kg	45.3	67.9	13.15	0.194	8.46	30.9	217	19.0	69.1	21.9	13.0	45.4	37.1	24.3	0.66	6.29	22.0	20.4	2.05	0.101	9.33	32.6	70.7	14.1	0.199
PCB 49	µg	µg/kg	38.2	57.2	2.76	0.048	7.41	29.0	190	18.1	71.0	20.9	10.3	43.7	29.6	16.2	0.55	6.07	25.6	19.7	1.63	0.083	7.27	30.7	55.1	5.59	0.101
PCB 52	µg	µg/kg	56.9	85.2	2.69	0.032	11.7	30.5	301	26.8	69.5	30.9	16.7	44.4	47.8	32.1	0.67	8.50	22.5	27.5	0.71	0.026	12.5	33.1	94.5	27.5	0.291
PCB 54	µg	µg/kg		<5.15					<10.6			<0.46	0.20	41.1	0.57	b	b	0.06		<0.45	b	b	0.22	46.2	1.70	b	b
PCB 66	µg	µg/kg	13.8	20.7	2.47	0.120	7.80	31.7	200	16.8	68.3	19.4	12.8	50.4	36.6	b	b	5.56	21.9	18.0	b	b	7.02	27.7	53.2	b	b
PCB 7	µg	µg/kg		<5.15					<10.6			<0.46	0.40	42.2	1.13	0.72	0.64	0.32	34.0	1.03	0.72	0.700	0.22	23.9	1.70	0.66	0.386
PCB 70	µg	µg/kg	50.3	75.5	6.08	0.081	10.1	31.7	259	21.7	68.3	25.1	14.4	43.3	41.1	26.3	0.64	8.16	24.6	26.4	3.11	0.118	10.7	32.2	81.0	14.5	0.179
PCB 8	µg	µg/kg	22.8	34.2	2.40	0.070	4.56	20.2	117	18.0	79.8	20.8	7.98	37.2	22.8	3.04	0.13	6.73	31.4	21.8	1.79	0.082	6.73	31.4	51.0	2.31	0.045
PCB 82	µg	µg/kg	18.3	27.4	3.54	0.129	3.68	38.8	94.4	5.81	61.2	6.71	1.57	37.9	4.49	3.01	0.67	1.17	28.3	3.80	0.85	0.224	1.40	33.8	10.6	1.40	0.132
PCB 86	µg	µg/kg	4.79	7.19	1.48	0.206	3.26	27.8	83.6	8.47	72.2	9.78	3.45	36.0	9.87	4.11	0.42	2.75	28.6	8.90	0.92	0.103	3.40	35.4	25.7	2.36	0.092
PCB 87	µg	µg/kg	16.4	24.7	0.21	0.009	4.95	34.8	127	9.27	65.2	10.7	3.86	33.3	11.0	2.84	0.26	3.43	29.6	11.1	1.47	0.133	4.30	37.1	32.6	1.93	0.059
PCB 97	µg	µg/kg	4.79	7.19	1.48	0.206	3.26	27.8	83.6	8.47	72.2	9.78	3.45	36.0	9.87	4.11	0.42	2.75	28.6	8.90	0.92	0.103	3.40	35.4	25.7	2.36	0.092
		Mean	25.4	38.1			Mean	31.6	123	Mean	70.0	11.5	Mean	39.3	13.9			Mean	27.4	10.4			Mean	34.0	28.4		
		Max	62.5	93.8			Max	41.0	327	Max	94.5	42.3	Max	50.4	50.6			Max	34.0	43.8			Max	46.2	148.1		
		Min	3.64	5.45			Min	20.2	10.7	Min	59.0	0.83	Min	33.3	0.57			Min	21.4	0.53			Min	23.9	0.73		
		SD	20.1	30.1			SD	4.73	102	SD	7.02	11.4	SD	4.29	16.4			SD	3.07	11.3			SD	4.46	35.9		

[a] Dry fraction mass, assuming a starting mass of 1 kg wet bulk sediment. Difference in dry sediment mass for sum of density fractions, sum of size fractions and bulk sediment are due to differences in moisture content assumed in smoothed mass balance.

[b] Unreplicated values

TABLE 6-2. New Bedford Mean PCB Mass and Concentration in Size and Density Fractions

	Units		Bulk				Density Fractions						Size Fractions													
							Bulk SG<2			Bulk SG>2			Sand					Silt					Clay			
	Mass	Conc	Mass	Concentration			Mass			Mass			Mass		Concentration			Mass		Concentration			Mass		Concentration		
				Conc	SD	COV	Mass	%	Conc[b]	Mass	%	Conc[b]	Mass	%	Conc	SD	COV	Mass	%	Conc	SD	COV	Mass	%	Conc	SD	COV
Sediment Mass	kg		0.395				0.120	13.3		0.780	86.7		0.135	35.1				0.162	42.1				0.088	22.9			
PCB1	µg	µg/kg		<8.70			15.24	22.9	127	51.3	77.1	65.8	11.0	40.2	81.5	3.61	0.044	4.06	14.9	25.05	1.20	0.048	12.3	44.9	139.5	27.8	0.199
PCB101	µg	µg/kg	3420	8647.5	541	0.063	956	25.7	7970	2770	74.3	3550	773	36.2	5730	83.2	0.015	419	19.6	2590	152	0.059	944	44.2	10700	1020	0.095
PCB103	µg	µg/kg	121	306.0	84.9	0.277	28.08	30.6	234	63.6	69.4	81.5	22.3	34.9	165	9.05	0.055	12.3	19.3	75.9	5.23	0.069	29.2	45.8	332	44.0	0.133
PCB114	µg	µg/kg	42.5	107.5	7.78	0.072	14.88	22.7	124	50.6	77.3	64.9	12.4	35.9	92.1	3.68	0.040	7.2	20.9	44.7	3.04	0.068	15.0	43.2	170	28.3	0.166
PCB118	µg	µg/kg	2550	6447.0	460	0.071	628	22.7	5230	2140	77.3	2740	713	37.1	5280	9.05	0.002	402	20.9	2480	110	0.044	808	42.0	9180	985	0.107
PCB126	µg	µg/kg	13.8	35.0	2.05	0.059	4.34	28.5	36.2	10.9	71.5	14.0	6.8	42.9	50.0	1.41	0.028	4.0	25.4	24.7	1.84	0.074	4.99	31.7	56.7	9.33	0.165
PCB128	µg	µg/kg	115	291.0	14.1	0.049	40.4	21.6	337	147	78.4	188	36.5	35.0	271	8.13	0.030	22.5	21.5	139	9.40	0.068	45.3	43.4	514	88.7	0.172
PCB136	µg	µg/kg	365	923.5	51.6	0.056	128	23.4	1070	420	76.6	538	103	35.6	759	24.0	0.032	52.7	18.3	326	22.3	0.068	132	46.0	1500	144	0.095
PCB137	µg	µg/kg	72.1	182.5	13.4	0.074	21.96	21.5	183	80.3	78.5	103	21.9	41.3	163	6.36	0.039	12.3	23.2	76.1	3.75	0.049	18.8	35.5	214	39.6	0.185
PCB138	µg	µg/kg	913	2310.0	141	0.061	290	22.2	2413	1010	77.8	1300	323	38.0	2390	60.3	0.025	177	20.8	1090	73.3	0.067	351	41.2	3980	408	0.102
PCB141	µg	µg/kg	141	356.0	25.5	0.072	28.8	22.0	240	102	78.0	131	31.8	38.7	236	7.42	0.031	18.0	21.8	111	7.99	0.072	32.5	39.5	369	14.7	0.040
PCB151	µg	µg/kg	374	947.0	163	0.172	99.2	22.4	827	343	77.6	440	104	37.6	768	32.3	0.042	53.4	19.4	330	21.8	0.066	119	43.0	1350	140	0.104
PCB156	µg	µg/kg	120	304.5	65.8	0.216	36.8	22.6	307	126	77.4	162	35.6	35.5	264	13.1	0.050	23.0	23.0	142	6.22	0.044	41.7	41.6	474	69.9	0.147
PCB167	µg	µg/kg	112	282.5	20.5	0.073	31.4	22.7	262	107	77.3	137	32.6	39.9	242	13.2	0.054	17.5	21.4	108	6.58	0.061	31.6	38.6	359	59.3	0.165
PCB170	µg	µg/kg	120	304.5	37.5	0.123	33.0	22.3	275	115	77.7	147	38.0	37.7	282	17.2	0.061	22.0	21.8	136	9.69	0.071	40.8	40.5	464	61.6	0.133
PCB18	µg	µg/kg	6190	15662.2	923	0.059	1690	22.5	14100	5840	77.5	7490	929	32.5	6880	524	0.076	508	17.8	3140	187	0.060	1420	49.7	16100	1430	0.089
PCB180	µg	µg/kg	201	507.5	24.7	0.049	55.3	22.4	461	191	77.6	245	70.0	42.5	519	14.8	0.028	38.1	23.1	235	14.6	0.062	56.5	34.3	642	111	0.173
PCB183	µg	µg/kg	63.6	161.0	5.66	0.035	22.7	22.5	189	78.0	77.5	100	22.3	38.4	166	8.77	0.053	12.5	21.5	77.2	4.38	0.057	23.3	40.1	265	42.8	0.161
PCB185	µg	µg/kg	13.8	35.0	2.83	0.081	4.37	20.1	36.4	17.4	79.9	22.3	5.4	39.7	39.9	0.28	0.007	2.90	21.4	17.9	0.71	0.040	5.29	39.0	60.1	11.0	0.184
PCB189	µg	µg/kg	11.2	28.4	1.27	0.045	1.57	16.9	13.1	7.72	83.1	9.90	2.80	36.9	20.8	0.35	0.017	1.94	25.6	12.0	0.71	0.059	2.85	37.5	32.4	7.07	0.218
PCB191	µg	µg/kg	9.5	24.1	2.05	0.085	1.06	24.4	8.80	3.28	75.6	4.20	2.30	40.3	17.0	0.42	0.025	1.70	29.9	10.5	2.97	0.283	1.69	29.8	19.3	4.74	0.246
PCB194	µg	µg/kg	30.2	76.5	2.83	0.037	9.14	39.3	76.2	14.1	60.7	18.1	11.4	42.3	84.6	6.08	0.072	6.2	23.2	38.6	3.18	0.083	9.3	34.5	106	18.5	0.175
PCB195	µg	µg/kg	12.6	32.0	2.33	0.073	3.54	21.8	29.5	12.7	78.2	16.3	6.5	39.4	48.4	3.25	0.067	3.75	22.6	23.2	1.77	0.076	6.28	37.9	71.4	14.8	0.207
PCB196	µg	µg/kg	14.4	36.4	2.83	0.078	3.82	21.9	31.8	13.6	78.1	17.4	6.1	40.1	44.9	2.83	0.063	3.20	21.2	19.8	1.34	0.068	5.87	38.8	66.7	20.3	0.304
PCB199	µg	µg/kg	7.5	19.0	1.70	0.089	2.12	19.8	17.7	8.58	80.2	11.0	2.61	38.5	19.4	0.78	0.040	1.36	20.1	8.40	0.28	0.034	2.81	41.4	31.9	3.96	0.124

(continued)

TABLE 6-2. (Continued)

	Units		Bulk				Density Fractions: Bulk SG<2			Density Fractions: Bulk SG>2			Size Fractions: Sand					Size Fractions: Silt					Size Fractions: Clay				
	Mass	Conc	Mass	Concentration			Mass			Mass			Mass		Concentration			Mass		Concentration			Mass		Concentration		
				Conc	SD	COV	Mass	%	Conc[b]	Mass	%	Conc[b]	Mass	%	Conc	SD	COV	Mass	%	Conc	SD	COV	Mass	%	Conc	SD	COV
PCB201	µg	µg/kg	26.4	66.8	3.54	0.053	6.53	21.0	54.4	24.5	79.0	31.4	9.9	39.5	73.0	4.67	0.064	5.7	22.8	35.2	2.05	0.058	9.4	37.6	107	16.3	0.153
PCB202	µg	µg/kg	8.0	20.3	1.27	0.063	3.06	20.4	25.5	11.9	79.6	15.3	3.26	38.1	24.2	5.16	0.214	1.73	20.2	10.7	0.14	0.013	3.57	41.7	40.6	11.1	0.274
PCB203	µg	µg/kg	16.1	40.9	1.77	0.043	5.77	22.4	48.1	20.0	77.6	25.7	10.6	44.1	78.2	5.02	0.064	5.7	23.6	34.9	2.26	0.065	7.7	32.2	87.7	18.5	0.211
PCB206	µg	µg/kg	17.2	43.5	5.44	0.125	4.15	23.0	34.6	13.9	77.0	17.8	7.2	44.2	53.7	5.44	0.101	4.03	24.6	24.9	0.92	0.037	5.12	31.2	58.2	10.3	0.176
PCB207	µg	µg/kg	3.89	9.85	2.05	0.208	0.73	14.8	6.10	4.21	85.2	5.40	1.33	38.1	9.85	2.19	0.223	0.93	26.7	5.75	0.07	0.012	1.23	35.3	14.0	3.11	0.222
PCB208	µg	µg/kg	7.4	18.85	1.63	0.086	1.19	22.7	9.90	4.06	77.3	5.20	3.35	45.9	24.9	1.91	0.077	1.71	23.4	10.6	0.64	0.060	2.24	30.7	25.5	8.77	0.344
PCB28	µg	µg/kg	8430	21400	1060	0.050	2120	22.0	17700	7510	78.0	9630	1450	30.7	10800	933.7	0.087	1000	21.2	6190	338.7	0.055	2270	48.1	25800	512.6	0.020
PCB40	µg	µg/kg	319	808	50.9	0.063	104	22.8	869	353	77.2	452	78.3	32.9	580	11.7	0.020	46.4	19.5	287	11.5	0.040	113	47.6	1290	121.9	0.095
PCB44	µg	µg/kg	2990	7570	467	0.062	896	25.7	7470	2590	74.3	3320	593	33.2	4390	131.1	0.030	332	18.6	2050	115.5	0.056	859	48.2	9760	905.5	0.093
PCB49	µg	µg/kg	7350	18600	1700	0.091	2120	22.5	17700	7320	77.5	9390	1250	33.1	9230	680.5	0.074	756	20.1	4670	418.9	0.090	1760	46.8	20000	19.0	0.001
PCB52	µg	µg/kg	7590	19200	1110	0.058	2080	22.2	17300	7260	77.8	9310	1240	33.8	9150	689.4	0.075	698	19.1	4310	244.7	0.057	1720	47.1	19600	9.76	0.000
PCB66	µg	µg/kg	1020	2590	179	0.069	572	23.7	4770	1840	76.3	2360	512	35.3	3800	148.5	0.039	312	21.5	1930	77.8	0.040	627	43.2	7130	70.7	0.010
PCB7	µg	µg/kg		<8.70			27.7	27.0	231	75.0	73.0	96.2	25.9	34.8	192	9.26	0.048	14.3	19.2	88.2	5.37	0.061	34.3	46.0	389	57.6	0.148
PCB70	µg	µg/kg	1720	4350	306	0.070	484	22.5	4030	1670	77.5	2140	438	34.7	3250	81.6	0.025	262	20.7	1620	94.5	0.058	565	44.7	6410	614.1	0.096
PCB8	µg	µg/kg	3580	9070	547	0.060	1020	26.0	8490	2900	74.0	3720	605	32.5	4480	194.7	0.043	351	18.9	2170	86.6	0.040	903	48.6	10300	896.3	0.087
PCB82	µg	µg/kg	77.6	197	12.0	0.061	24.5	25.1	204	73.2	74.9	93.9	17.5	32.4	130	6.51	0.050	11.1	20.5	68.3	2.55	0.037	25.4	47.1	289	63.0	0.218
PCB86	µg	µg/kg					295	22.3	2460	1030	77.7	1320	274	35.7	2030	42.4	0.021	149	19.5	922	59.4	0.064	344	44.8	3910	367.7	0.094
PCB87	µg	µg/kg	232	588	32.5	0.055	60.1	21.9	501	215	78.1	275	70.1	34.5	519	4.6	0.009	44.3	21.8	273	33.9	0.124	88.8	43.7	1010	108.4	0.107
PCB97	µg	µg/kg	361	913	41.0	0.045	295	22.3	2460	1030	77.7	1320	285	35.7	2110	47.6	0.023	155	19.5	958	63.3	0.066	357	44.8	4060	388.7	0.096
		Mean	1190	3010			Mean	23.1	2700	Mean	76.9	1390	Mean	37.4	1720			Mean	21.4	839			Mean	41.2	3580		
		Max	8430	21400			Max	39.3	17700	Max	85.2	9630	Max	45.9	10800			Max	29.9	6190			Max	49.7	25800		
		Min	3.89	9.85			Min	14.8	6.10	Min	60.7	4.20	Min	30.7	9.85			Min	14.9	5.75			Min	29.8	14.0		
		SD	2280	5780			SD	3.6	5020	SD	3.6	2640	SD	3.6	2830			SD	2.6	1440			SD	5.4	6280		

[a] Dry fraction mass, assuming a starting mass of 1 kg wet bulk sediment. Difference in dry sediment mass for sum of density fractions, sum of size fractions and bulk sediment are due to differences in moisture content assumed in smoothed mass balance.

[b] Unreplicated values

TABLE 6-3. New York Mean PCB Mass and Concentration in Size and Density Fractions

	Units		Bulk				Density Fractions						Size Fractions													
							Bulk SG<2			Bulk SG>2			Sand					Silt					Clay				
	Mass	Conc	Mass	Concentration			Mass			Mass			Mass		Concentration			Mass		Concentration			Mass		Concentration		
				Conc	SD	COV	Mass	%	Conc[b]	Mass	%	Conc[b]	Mass	%	Conc	SD	COV	Mass	%	Conc	SD	COV	Mass	%	Conc	SD	COV
Sediment Mass	kg		0.367				0.027	10.8		0.223	89.2		0.117	23.3				0.111	22.1				0.274	54.6			
PCB101	µg	µg/kg	13.0	35.4	3.75	0.106	2.9	20.2	107	11.4	79.8	51.2	3.4	29.8	28.8	5.94	0.206	1.58	14.0	14.2	0.57	0.040	6.34	56.2	23.2	2.76	0.119
PCB118	µg	µg/kg	11.9	32.6	2.33	0.072	2.2	19.7	80.6	8.9	80.3	39.7	3.00	26.9	25.6	2.83	0.110	1.80	16.1	16.2	0.42	0.026	6.34	57.0	23.2	0.64	0.027
PCB128	µg	µg/kg		<4.6			0.6	35.9	22.7	1.09	64.1	4.90	0.45	29.6	3.85	0.07	0.018	0.22	14.6	2.00	0.00	0.000	0.85	55.8	3.10	0.28	0.091
PCB138	µg	µg/kg	10.4	28.3	0.92	0.033	2.8	31.3	103	6.10	68.7	27.4	2.66	30.2	22.7	0.28	0.012	1.43	16.2	12.9	0.07	0.006	4.70	53.5	17.2	0.92	0.054
PCB141	µg	µg/kg	2.1	5.86	0.30	0.052	0.61	37.9	22.7	1.00	62.1	4.50	0.81	33.5	6.90	0.28	0.041	0.37	15.2	3.30	0.85	0.257	1.23	51.2	4.50	0.14	0.031
PCB151	µg	µg/kg	3.4	9.24	1.64	0.178	0.8	29.2	29.7	1.94	70.8	8.70	0.89	32.1	7.60	1.27	0.167	0.40	14.4	3.60	0.00	0.000	1.48	53.4	5.40	0.57	0.105
PCB156	µg	µg/kg		<4.6			0.3	30.5	10.5	0.65	69.5	2.90	0.30	28.3	2.60	0.42	0.163	0.18	17.0	1.65	0.07	0.043	0.59	54.7	2.15	0.07	0.033
PCB167	µg	µg/kg		<4.6			0.2	29.2	8.50	0.56	70.8	2.50	0.13	27.2	1.15	0.35	0.307	0.10	20.2	0.90	0.28	0.314	0.26	52.6	0.95	0.21	0.223
PCB170	µg	µg/kg	2.3	6.38	0.10	0.016	0.5	33.0	20.3	1.12	67.0	5.00	0.77	29.6	6.60	1.84	0.279	0.41	15.7	3.70	0.14	0.038	1.42	54.6	5.20	0.14	0.027
PCB18	µg	µg/kg	12.9	35.0	3.25	0.093	1.5	7.8	54.2	17.3	92.2	77.7	1.81	18.7	15.5	0.57	0.036	1.06	10.9	9.55	0.21	0.022	6.81	70.3	24.9	0.64	0.026
PCB180	µg	µg/kg	5.1	14.0	0.35	0.025	1.7	41.6	61.2	2.32	58.4	10.4	2.48	43.8	21.2	13.72	0.647	0.81	14.3	7.30	0.57	0.077	2.37	41.9	8.65	0.21	0.025
PCB183	µg	µg/kg		<4.6			0.44	33.6	16.3	0.87	66.4	3.90	0.63	39.8	5.40	3.11	0.576	0.23	14.4	2.05	0.07	0.034	0.73	45.8	2.65	0.21	0.080
PCB185	µg	µg/kg		<4.6			0.15	30.7	5.50	0.33	69.3	1.50	0.33	39.8	2.80	1.56	0.556	0.14	16.9	1.25	0.21	0.170	0.36	43.3	1.30	0.14	0.109
PCB189	µg	µg/kg		<4.6			0.16	53.9	5.80			<0.66	0.15	39.7	1.25	0.49	0.396			<0.48					<0.80		
PCB194	µg	µg/kg		<4.6			0.47	46.9	17.5	0.54	53.1	2.40	1.39	63.1	11.9	12.0	1.008	0.25	11.4	2.25	0.21	0.094	0.56	25.6	2.05	0.21	0.103
PCB195	µg	µg/kg		<4.6			0.13	35.0	4.90	0.25	65.0	1.10	0.35	46.7	2.95	2.62	0.887	0.11	14.3	0.95	0.07	0.074	0.29	39.0	1.05	0.07	0.067
PCB196	µg	µg/kg		<4.6			0.28	48.7	10.2	0.29	51.3	1.30	0.95	61.6	8.10	6.65	0.821	0.17	10.8	1.50	0.14	0.094	0.42	27.6	1.55	0.21	0.137
PCB199	µg	µg/kg		<4.6			0.09	51.4	3.50			<0.66	0.29	55.1	2.45	2.33	0.952	0.06	10.7	0.50	0.14	0.283			<0.80		
PCB201	µg	µg/kg	1.7	4.64	0.72	0.155	0.68	47.8	25.0	0.74	52.2	3.30	1.94	64.8	16.6	15.6	0.944	0.28	9.5	2.55	0.21	0.083	0.77	25.7	2.80	0.28	0.101
PCB202	µg	µg/kg		<4.6			0.17	46.3	6.40	0.20	53.7	0.90	0.38	56.2	3.25	2.62	0.805	0.08	11.5	0.70	0.14	0.202	0.22	32.4	0.80	0.00	0.000
PCB203	µg	µg/kg		<4.6			0.42	38.3	15.4	0.67	61.7	3.00	1.56	65.4	13.3	11.9	0.893	0.22	9.3	2.00	0.28	0.141	0.60	25.3	2.20	0.14	0.064
PCB206	µg	µg/kg		<4.6			0.65	52.8	24.0	0.58	47.2	2.60	1.60	67.6	13.7	12.8	0.938	0.21	8.7	1.85	0.07	0.038	0.56	23.8	2.05	0.07	0.034
PCB207	µg	µg/kg		<4.6			0.09	37.0	3.40	0.16	63.0	0.70	0.22	71.1	1.85	1.63	0.879			<0.48					<0.80		
PCB208	µg	µg/kg		<4.6			0.44	100.0	16.2	0.00	0.0		0.73	59.0	6.20	4.24	0.684	0.16	13.1	1.45	0.21	0.146	0.34	27.9	1.25	0.21	0.170

(continued)

TABLE 6-3. (Continued)

	Units		Bulk				Density Fractions: Bulk SG<2			Density Fractions: Bulk SG>2			Size Fractions: Sand					Size Fractions: Silt					Size Fractions: Clay				
	Mass	Conc	Mass	Concentration			Mass			Mass			Mass		Concentration			Mass		Concentration			Mass		Concentration		
				Conc	SD	COV	Mass	%	Conc[b]	Mass	%	Conc[b]	Mass	%	Conc	SD	COV	Mass	%	Conc	SD	COV	Mass	%	Conc	SD	COV
PCB28	µg	µg/kg	20.0	54.5	3.54	0.065	3.7	11.5	136	28.3	88.5	127	3.01	17.2	25.7	2.40	0.094	2.30	13.2	20.8	1.20	0.058	12.2	69.6	44.4	1.77	0.040
PCB40	µg	µg/kg	4.7	12.8	0.07	0.006	0.5	22.0	19.1	1.83	78.0	8.20	0.75	32.1	6.40	0.85	0.133	0.26	10.9	2.30	0.14	0.061	1.33	57.0	4.85	0.21	0.044
PCB44	µg	µg/kg	13.3	36.3	1.34	0.037	2.1	18.1	77.7	9.5	81.9	42.6	2.59	25.6	22.1	0.14	0.006	1.19	11.8	10.8	0.78	0.072	6.30	62.5	23.0	0.99	0.043
PCB49	µg	µg/kg	16.7	45.5	8.77	0.193	2.0	7.9	75.6	23.6	92.1	106	2.23	19.8	19.1	1.06	0.056	1.55	13.8	14.0	0.71	0.051	7.47	66.4	27.3	0.64	0.023
PCB52	µg	µg/kg	24.3	66.1	3.54	0.053			<0.84	24.8	100	111	3.12	22.9	26.7	0.92	0.034	1.71	12.6	15.5	0.35	0.023	8.77	64.5	32.0	1.56	0.049
PCB66	µg	µg/kg	13.3	36.4	4.17	0.115	6.7	29.1	249	16.3	70.9	73.3	10.2	37.2	87.4	19.23	0.220	2.81	10.2	25.4	0.35	0.014	14.4	52.5	52.7	0.64	0.012
PCB7	µg	µg/kg					0.04	15.8	1.40	0.20	84.2	0.90			<0.68					<0.48					<0.80		
PCB70	µg	µg/kg	16.1	43.9	3.39	0.077	3.3	28.2	124	8.5	71.8	38.3	3.18	29.5	27.2	0.64	0.023	1.38	12.9	12.5	1.34	0.108	6.19	57.6	22.6	4.10	0.181
PCB8	µg	µg/kg	6.1	16.6	1.20	0.073	0.7	8.2	25.2	7.6	91.8	34.0	0.46	9.2	3.95	1.20	0.304	0.53	10.6	4.80	0.00	0.000	4.06	80.3	14.8	0.99	0.067
PCB82	µg	µg/kg	4.3	11.7	0.42	0.036	0.64	39.6	23.8	0.98	60.4	4.40	0.74	33.0	6.30	0.85	0.135	0.37	16.7	3.35	0.49	0.148	1.12	50.3	4.10	0.71	0.172
PCB86	µg	µg/kg					1.2	19.5	43.7	4.9	80.5	21.8	1.23	27.8	10.6	0.35	0.034	0.61	13.7	5.49	0.05	0.009	2.59	58.4	9.46	0.69	0.073
PCB97	µg	µg/kg		<4.6			1.2	19.5	43.7	4.9	80.5	21.8	1.25	27.9	10.7	0.35	0.033	0.62	13.8	5.55	0.07	0.013	2.60	58.3	9.50	0.71	0.074
		Mean	10.1	27.5			Mean	33.1	42.7	Mean	71.1	25.6	Mean	38.3	13.7			Mean	13.3	6.40			Mean	49.8	11.9		
		Max	24.3	66.1			Max	100	249	Max	100	127	Max	71.1	87.4			Max	20.2	25.4			Max	80.3	52.7		
		Min	1.70	4.64			Min	7.80	1.40	Min	7.80	0.70	Min	9.2	1.15			Min	8.70	0.50			Min	23.8	0.80		
		SD	6.70	18.2			SD	17.5	51.3	SD	17.5	35.4	SD	16.4	15.5			SD	2.63	6.53			SD	14.8	13.5		

[a] Dry fraction mass, assuming a starting mass of 1 kg wet bulk sediment. Difference in dry sediment mass for sum of density fractions, sum of size fractions and bulk sediment are due to differences in moisture content assumed in smoothed mass balance.

[b] Unreplicated values

DISCUSSION

Clay appears to play a larger role in PCBs sorption than for PAHs. Mean mass PCBs reporting to the mineral fraction was higher than mass percent of PAHs, for all three sediments. Further, contaminant concentrations were two to four times higher in the clay fraction of New Bedford, than in either the silt or sand fractions, and two to three times higher in the clay fraction for Calumet. Distribution was slightly different with New York, where highest contaminant concentration was in the sand, but only slightly higher than in the clay fraction. The relative influence of organic and clay materials is difficult to determine without statistical analysis. However, comparison of the organic and mineral fraction concentrations for the New Bedford sediment suggests that clay minerals are at least partly responsible for the high PCBs concentrations observed in the clay fraction for this sediment. Contaminant concentrations in the organic fraction were approximately twice that of the mineral fraction in New Bedford, while contaminant concentrations in the clay fraction were over four times that in the silt, suggesting organics may not fully explain the high concentrations seen in the clay fraction. There were also some PCBs present at higher concentrations in the mineral fraction than in the organic fraction, suggesting an association with either hard carbon or clay mineral phases, rather than natural organic material of low density. The observed distribution seems most consistent with sorption to the external surfaces of the clay, for the following reasons: Molecular volume of PCBs ranges from approximately 177 to 323 $Å^3$ (Mackay, Shiu and Ma 1992). The larger PCBs are too big to be accommodated in the clay mineral silicate pores (10-20 Å) or soot pores (<4-10 Å) (Cornelissen et al 2004). Moreover, while both may play a role, surface sorption to soot is unlikely to be as important as surface sorption to clay, given their respective surface areas. Specific surface area of soot was estimated to range from 58 m^2/g (Lastoskie and Gubbins 2000 as cited in Cornelissen et al. 2004) to 100 m^2/g (Gustafsson and Gschwend 1997). Internal surface area of vermiculite, for example, was estimated to range from 570-700 m^2/g (Hwang and Cutright 2004). Large PCBs may sorb primarily to the outer surface of clays through interaction between the dipole moment of the PCBs and the clay surface charge. Smaller PCBs could exchange in the clay interlayers as well.

High concentrations of contaminants in the sand fraction are thought to be due to either a coarse (non-black carbon) organic phase, hard carbon phase, or an oil and grease phase. Correlations between PCBs, OG, soot and OC will be further explored using statistical techniques in Chapter 7.

Some general relationships can be derived based on the results of the fractionation study which are of utility in assessing feasibility of contaminant reduction by size or density separation. Final contaminant concentration resulting from removal of a selected size or density fraction can be expressed as:

$$C_F = C_I * \left(\frac{1 - f_i}{1 - f_{sed}} \right) \qquad (6\text{-}1)$$

where

f_i = fraction contaminant mass in size or density fraction removed
f_{sed} = fraction of sediment mass comprised by size or density fraction removed
C_I = contaminant concentration in bulk sediment, µg/kg

C_F = contaminant concentration in treated sediment, μg/kg

The percent reduction (R) in contaminant concentration is given by

$$R = \left(1 - \left(\frac{1 - f_i}{1 - f_{sed}}\right) * 100\right) \quad (6\text{-}2)$$

A summary of the contaminant reduction resulting from removal of operationally defined clay and organic fractions for the three sediments studied is given in Table 6-4. Negative values indicate that higher concentrations would be expected in the treated sediment than in the untreated sediment. If the proportionality in Equation 6-1 is greater than 1, higher concentrations will result in the residuals. For Calumet, there were no instances where higher concentrations were predicted in the treated sediment. Highest mean reduction of PCBs resulted from removal of the organic fraction, but removal of the clay fraction would result in nearly comparable contaminant reduction. For New Bedford, removal of the clay resulted in positive contaminant reduction for all PCBs, as did removal of the organic fraction. Mean contaminant reduction in New Bedford was higher with removal of the clay fraction, however. For New York, removal of the clay fraction resulted in negative reduction for 20 of 36 PCBs. Removal of the organic fraction resulted in negative reduction for four PCBs, but a positive mean reduction overall.

TABLE 6-4. Percent reduction in PCB concentration (R) with removal of selected operationally defined fractions

	Clay Fraction Removed			Organic Fraction Removed		
Sediment	**Min[a]**	**Max[a]**	**Mean[b]**	**Min[a]**	**Max[a]**	**Mean[b]**
Calumet	8.6	57.2	21.6	1.3	68.0	29.2
New Bedford	9	34.8	23.8	1.7	30	11.3
New York	-80.6	81.6	-10.9	-12.1	100	24.0

[a] Minimum or maximum percent removal for an individual compound
[b] Mean percent removal for all PCBs

SUMMARY AND CONCLUSIONS

Both clay and organic fractions appear to be important to PCB sorption for these sediments to varying degrees. Higher contaminant reduction appears to be achievable with removal of the operationally defined clay fraction for PCBs than was reported for PAHs in Chapter 5. Conversely, PCBs reduction with removal of the organic fraction, while still appreciable for two sediments, was lower for PCBs than for PAHs for all three sediments.

PCBs present at higher concentrations in the mineral fraction than in the organic fraction suggest an association with higher density hard carbon phases or clay mineral phases, rather than natural organic material of low density. Such materials may be difficult to separate from similar

size mineral particles using physical separation, as density differences may not be sufficient for the process to discriminate. Certainly, particulate associated contaminants cannot be separated from clean sediment using a screening method alone where particle sizes are similar. Separation processes such as a hydrocyclone or upflow column are typically needed to capitalize on density differences as well. Correlation of contaminant concentrations to sorptive phases is therefore potentially very important to designing a successful treatment train. Fractionation studies provide a good foundation for this, but may need to be augmented with more rigorous statistical analysis in order to evaluate a particular contaminant distribution trend and obtain phase specific contaminant concentrations.

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CHAPTER 7

PAH AND PCB DISTRIBUTION WITH RESPECT TO SORPTIVE PHASES IN NATURAL SEDIMENTS – CORRELATIONS

INTRODUCTION

The mobility and bioavailability of contaminants present in navigation sediments is typically evaluated using partitioning analysis (USEPA/USACE 1991, 1998; USACE 2003). Fundamental to partitioning analysis is an understanding of the distribution of the contaminants between solid and aqueous phases. Distribution coefficients are typically calculated from bulk sediment and contaminant properties (theoretical coefficients), or from measured bulk sediment and pore water concentrations (observed coefficients) (DiToro et al. 1991; EPA 1999). These methods produce a distribution coefficient representative of the composite sediment, but offer no information regarding the relative distribution between the different sorptive phases present. Such information may be very important to assessment of contaminant bioavailability, and effectiveness of potential treatments, such as separation. Direct measurement of phase specific contaminant concentrations is not practical however, due to the difficulty of separating the sorptive phases while preserving the contaminant distribution. Further, correlation of contaminant distribution to different sediment fractions is typically problematic. Conservative values are often selected for lack of better information, and in an effort to be environmentally protective.

Carbon phases present in sediment may be quite variable in character, however, with specific gravity slightly below or slightly above that of water (broken bituminous coal, charcoal, cinders and coal tar, for example) to approximately 2.1 (activated carbon, graphite). Distribution coefficients have been developed for soot based on sorption studies with commercial carbon sorbents or natural sediments, and using thermodynamic properties of contaminants and carbon bearing phases (Cornelissen et al. 2004a,b; Jonker and Koelmans 2002; van Noort 2003; Bucheli & Gustafsson 2000; Walters & Luthy 1984). Many of these values have been obtained from sorption studies conducted on a single sorbent phase or on sediments in which competing phases have been removed as completely as possible. Few environmental values are available for natural sediments, where sorption takes place in the presence of other sorptive phases. Cornelissen et al. (2004a) reported environmental values for select PAHs and PCBs, and concluded that sorption to black carbon phases was inhibited by native PAHs and natural organic matter. Cornelissen et al. (2004a) also reported the only non-black carbon organic carbon coefficients found in the literature.

In this phase of the study, fractionation data obtained on three natural sediments was used to obtain correlations between contaminant distribution and distribution of the major sorptive phases present. Mass of oil and grease, soot, (non-black carbon) organic carbon and clay were correlated to the observed contaminant mass distribution by regression. This study is unique in the respect that multiple sorptive phases were accounted for. Phase specific contaminant concentrations obtained in this manner will be used to develop partitioning coefficients reflective of sorption occurring in natural sediments, under environmental conditions, and in the presence of competitive sorptive phases.

APPROACH

Contaminant distribution data was obtained previously in a fractionation study of 3 natural sediments from sites in Calumet River, New York Harbor and New Bedford Harbor (Chapters 5 and 6). In that study, PAH and PCB concentrations were measured in 3 size and 2 density fractions of each sediment and in the bulk sediment. Concentration of four sorptive phases, oil and grease (OG), soot, organic carbon (OC) and clay were also measured.

Initial efforts to obtain correlations between contaminant concentration or mass and the sorptive phases using the fractionation data were problematic. Stepwise regression of the PAH data produced models with only one phase parameter meeting the significance criteria (p value ≤ 0.15) for inclusion in the model. For some compounds, no parameters were found to be significant. This outcome is inconsistent with at least some sorption occurring in one or more phases. As this could be attributable to non-linearity of the relationship, various transforms were evaluated. Correlation coefficients were used as screening tools to identify the transforms producing the most linear relationship between the contaminant data and the sorptive phases. These transforms were then tested in the stepwise regression, but this was also largely unsuccessful in producing models inclusive of all independent variables.

The influence of each variable was evaluated, by generating a coefficient and p value for each independent variable, whether or not statistically significant as defined by the p value. Seven models were evaluated: PAH vs. each independent variable (OG, Soot and OC) individually, and PAH vs. all possible combinations of the variables. Regressions on single variable models (e.g. MPAH = MOG) often produced positive coefficients for each of the independent variables, with high R^2 values in many cases. However, in the combined model (e.g. MPAH = MOG MSOOT MOC), which is of most interest here, coefficients that were positive in the single variable model sometimes became negative in the full model.

Mass ratios of the sorptive phases were also compared to the mass ratios of the contaminants. The resulting values seem to suggest which phase dominated the contaminant distribution, but in some cases they appeared to be contradictory, depending upon which size or density fractions were used in the comparison.

Because none of the previous analysis resulted in a consistent outcome for all of the sediments used in the study, the mass balance was re-visited to ascertain whether there was some fundamental problem in the assumptions used to reconstruct the mass balance (Chapter 5), or in the analytical results, contributing to the difficulty with the statistical analysis. Use of the contaminant mass to refine the sediment mass balance provided a further check on the basis of the mass balance. There were four samples taken from the homogenized sediment for characterization and processing, two bulk sediment samples, a sample for size fractionation and a sample for density fractionation. (Size and density replicates were taken after separation.) Contaminant concentrations in size fractions were corrected for losses due to solubilization occurring during separation. Plots of the contaminant mass in the size and density fractions were then compared to the contaminant mass in the bulk sediment, where an approximate one to one correspondence was expected. Bias in the results could readily be seen in some plots. These differences may be attributable to variability in sample preparation or analysis, for samples run in different batches. Variability of sediment properties assumed in the mass balance calculations may also contribute. Based on these assumptions, the following data-conditioning step was developed and used to refine the sediment mass balance.

Total contaminant mass in sediment fractions was calculated by taking the contaminant concentration measured in each of the fractions times the estimated mass of those fractions. Contaminant mass for the size fractions and density fractions were summed, and the means compared to each other and to the bulk sediment. Results obtained for PAHs from the initial reconstructed mass balance are pictured for Calumet in Figures 7-1, 7-2 and 7-3. These plots demonstrate that the data is relatively consistent, but possibly biased due to analytical variability or variability in sediment properties assumed in reconstructing the sediment mass balance. The plots are linear, as expected, with high R^2 and few outliers (extreme outliers have been removed from these plots), but they are not one to one. For Calumet, PAH mass calculated for the size and density fractions is consistently less than that measured in the bulk sediment. The sediment mass balance was adjusted to address the observed bias prior to statistical analysis, using the following procedure.

The reconstructed mass balance calculations assumed a starting mass of 1 kg wet sediment. It was also assumed that the following parameters were essentially equivalent for subsamples of the homogenized sediment:

- Contaminant concentration
- Concentration of oil and grease, soot and total organic carbon
- Grain size

The moisture content initially used in the mass balance calculations was the value measured for the homogenized bulk sediment. The moisture content could vary over time however, with repeated handling of the sediment and exposure to the atmosphere. The assumption was therefore made that the moisture content was the most mobile phase, and this parameter was varied in order to adjust the mass balance. By altering the moisture content, the mass dry solids of the starting sample changes, as does the dry mass reporting to the respective size and density fractions, but the respective mass distribution between the fractions is not greatly altered. This is illustrated in Table 7-1. By adjusting the moisture content as indicated in the table, the smoothed mass balance is obtained, resulting in a better correspondence between the composite contaminant mass obtained for the size and density fractions and the bulk sediment (Figures 7-4, 7-5 and 7-6). Effectively, this produces samples with equivalent contaminant mass, rather than equivalent sediment mass. The specific steps of this procedure were as follows:

- Total wet sediment mass of 1 kg assumed for each aliquot (size fractionation, density fractionation and bulk sediment subsamples)
- Moisture content of homogenized bulk sediment was assumed
- Dry sediment mass was calculated based on assumed moisture content
- Mass of size and density fractions was calculated as previously described (Chapter 5, Equations 5-1 through 5-10)
- Contaminant mass was calculated for each fraction based on measured contaminant concentration in each fraction, and sediment mass calculated in previous step
- Mean total contaminant mass for size fractions was plotted against mean bulk sediment contaminant mass

- Mean total contaminant mass for density fractions was plotted against mean bulk sediment contaminant mass
- Mean total contaminant mass for size fractions was plotted against mean total contaminant mass for density fractions
- Plots were fitted with linear trendlines
- Moisture content was adjusted for each fraction until trendline coefficient was approximately equal to one for each plot

Further, an entropy based regression procedure applicable to ill-conditioned data was employed in subsequent analysis. The procedure fits linear regression models using a technique that uses prior assumptions about the parameters and errors to obtain parameter estimates. Estimates obtained by this method are biased, but variances are small as compared to results obtained from traditional regression methods. The method is reported to be more robust than conventional regression for data sets where some distributional assumptions are violated, as when outliers are present, when regressors in the model are highly correlated, when there are fewer observations than parameters to estimate, or when parameter estimates obtained from more traditional methods are not logical (Personal communication SAS Technical Support August 04, 2004). Entropy procedures are used to solve economics problems where the desired parameter cannot be measured, and only non-experimental observational data is available (Golan et al 1996). This is essentially analogous to the problem of estimating phase specific concentrations when the phases cannot be effectively separated for direct measurement of contaminant concentration. The fractionation data sets are also good candidates for this procedure as they evidence some non-normality, collinearity, and instability of variance. Additionally, conventional regression methods produced negative coefficients having no physical significance.

The modified contaminant distribution data (based on the adjusted mass balance) was analyzed using PROC ENTROPY in SAS, a commercial statistical analysis package. The model statements evaluated were as follows, with the transforms selected from evaluation of correlation coefficients as previously described:

Model A: $M_i = b_1 M_{OG} + b_2 M_{SOOT} + b_3 M_{OC}$

Model B: $M_i = b_1 M_{OG} + b_2 M_{SOOT} + b_3 M_{OC} + b_4 M_{CLAY}$

Model C: $M_i = b_1 \sqrt[3]{M_{OG}} + b_2 \sqrt[3]{M_{SOOT}} + b_3 \sqrt[3]{M_{OC}}$

Model D: $M_i = b_1 \sqrt[3]{M_{OG}} + b_2 \sqrt[3]{M_{SOOT}} + b_3 \sqrt[3]{M_{OC}} + b_4 M_{CLAY}$

Model BMC: $M_i = b_1 M_{OG} + b_2 M_{SOOT} + b_3 M_{OC} + b_4 M_{MINCLAY}$

Model DMC: $M_i = b_1 \sqrt[3]{M_{OG}} + b_2 \sqrt[3]{M_{SOOT}} + b_3 \sqrt[3]{M_{OC}} + b_4 M_{MINCLAY}$

M_i is the measured mass of PAH or PCB in the bulk sediment or sediment fraction. Coefficients obtained by the regression represent the phase specific contaminant concentrations or a function from which the concentrations can be calculated. M_{CLAY} represents the mass of material 5μm in size or smaller, as measured on a Coulter Counter. The <5 μm material may actually include non-mineral particles such as colloidal organics and soot. $M_{MINCLAY}$ represents the mineral portion of the <5 μm fraction. Fraction samples were treated to remove organic carbon and soot by heating the samples in a muffle furnace at 350º for 24 hours, then separating the residuals in heavy media at a specific gravity (S.G.) of 2.0. The heavy materials (with S.G.>2.0) were

retained for size analysis on the Coulter Counter and the mass mineral clay estimated from the resulting size distribution.

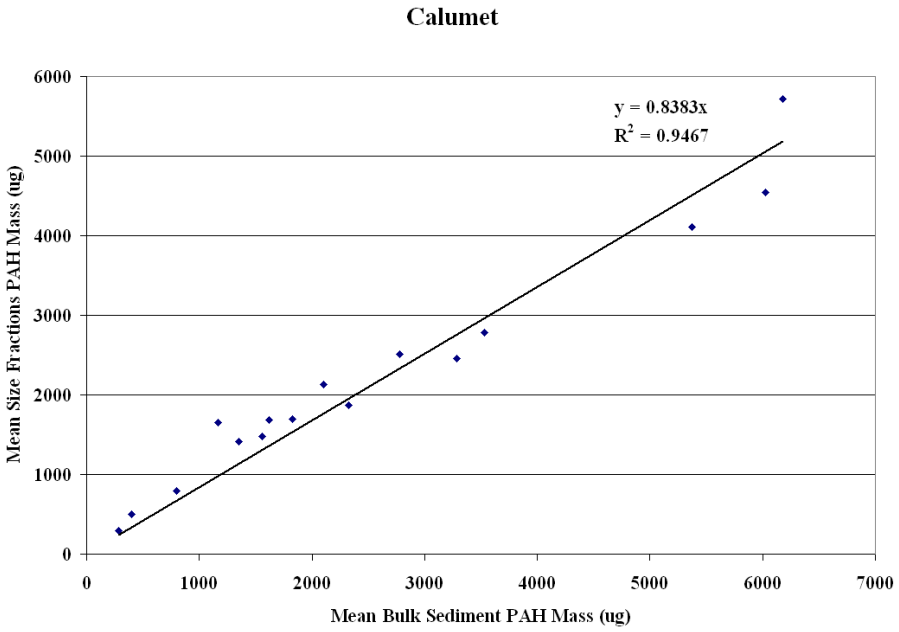

FIGURE 7-1. Calumet composite PAH contaminant mass for size fractions versus bulk sediment original reconstructed mass balance.

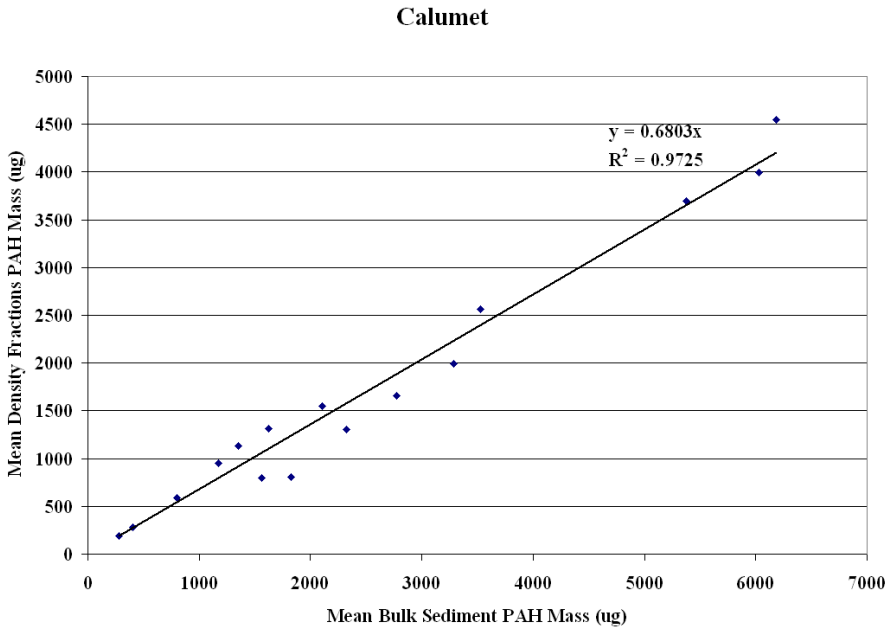

FIGURE 7-2. Calumet composite PAH contaminant mass for density fractions versus bulk sediment original reconstructed mass balance.

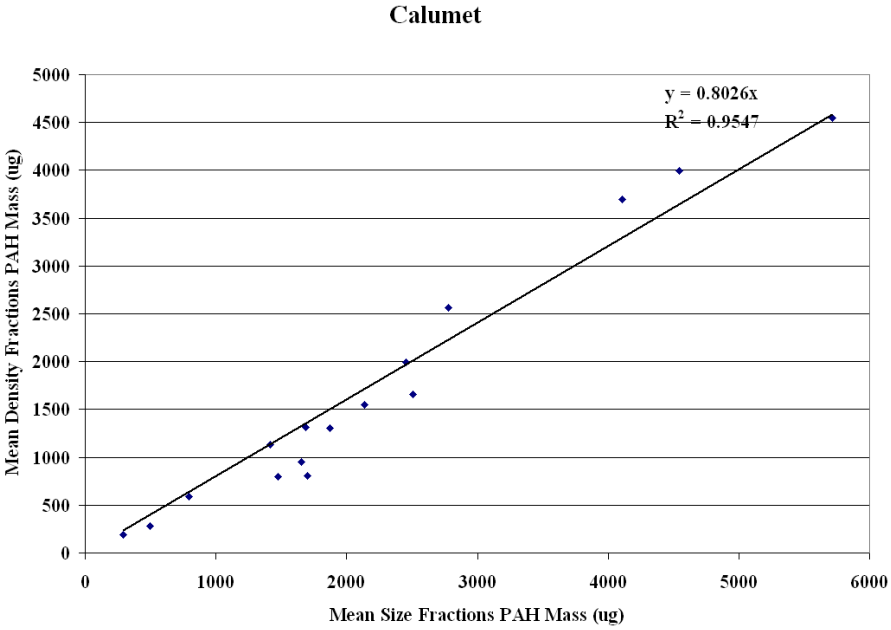

FIGURE 7-3. Calumet composite PAH contaminant mass for density fractions versus size fractions original reconstructed mass balance.

TABLE 7-1. Calumet PAH Sediment Distribution for Reconstructed and Smoothed Mass Balance

		Sediment Mass Dry Weight (kg)											
	MC[1]	Bulk		Org		Min		Sand		Silt		Clay	
	%	Wet Wt	Dry Wt	Dry Wt	% Mass	Dry Wt	% Mass	Dry Wt[2]	% Mass	Dry Wt	% Mass	Dry Wt	% Mass
Initial Distribution	33.3	1	0.636	0.027	4.2	0.609	95.8	0.282	44.3	0.248	39.0	0.106	16.7
Adjusted Distribution	17	1	0.791					0.350	44.2	0.309	39.1	0.132	16.7
	5	1	0.905	0.039	4.3	0.866	95.7						

[1] Moisture content
[2] Less mass of gravel fraction (.031 kg).

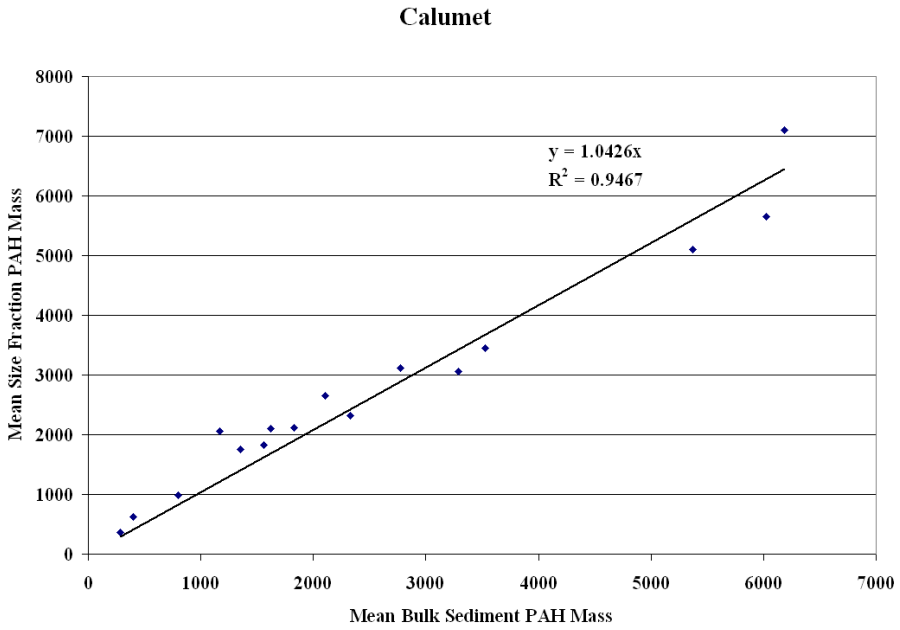

FIGURE 7-4. Calumet composite PAH contaminant mass for size fractions versus bulk sediment adjusted sediment mass balance.

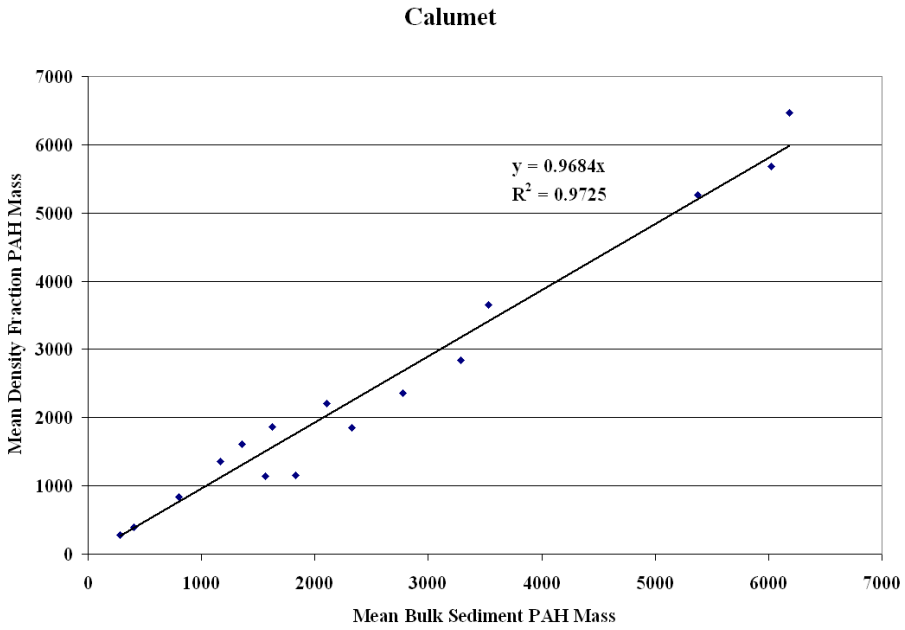

FIGURE 7-5. Calumet composite PAH contaminant mass for density fractions versus bulk sediment adjusted sediment mass balance.

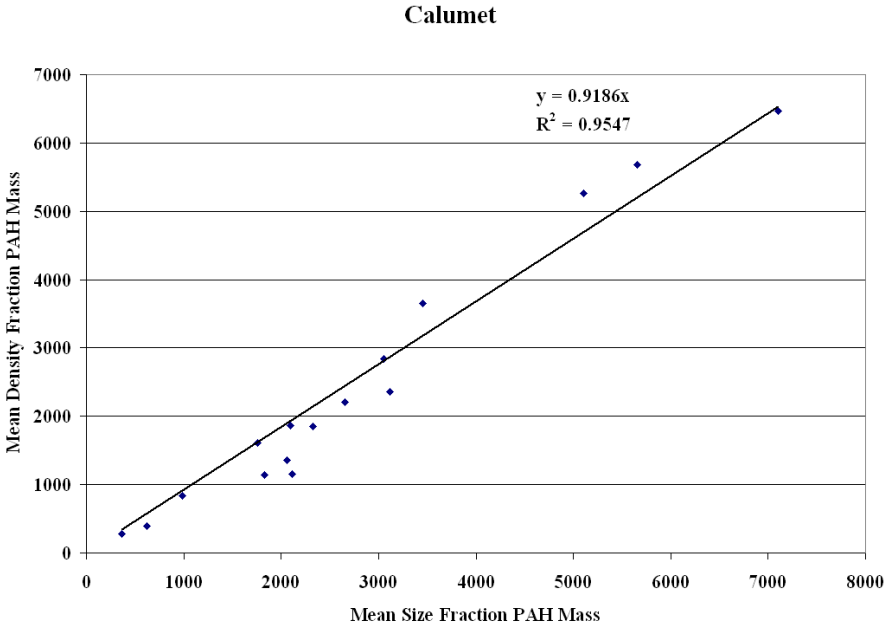

FIGURE 7-6. Calumet composite PAH contaminant mass for density fractions versus size fractions adjusted sediment mass balance.

With PROC ENTROPY, it was possible to simultaneously constrain the model intercept to zero and the parameters to positive values. This was important as conventional regression procedures frequently returned negative values for one or more regression coefficients and the intercept, which was not physically meaningful. By constraining the intercept to zero and parameters to positive values, the variance is then apportioned among the specified phases, rather than to a constant that may have no physical meaning. These are considered to be reasonable constraints to the analysis if the major sorptive phases have been identified and included in the model. In order to assess the utility of the coefficients obtained with ENTROPY, parameter estimates were checked by plotting contaminant mass in the sorptive phases, calculated using the regression coefficients obtained with ENTROPY, against measured contaminant mass in the fractions and the bulk sediment. Linear regression was performed on the model $M_{i\ Predicted} = M_{i\ Measured}$, to evaluate the models as predictors. A paired t test was used to assess the equality of the predicted and measured values for each model. Normality of the difference values was first evaluated with the Shapiro-Wilke test. Then, contaminant mass predicted for the sorptive phases by the best fit model was tabulated and compared to the measured contaminant mass in the bulk sediment.

The principal considerations in model selection included consistency between measures of goodness of fit, parameter significance, consistency between the full data set and the bulk sediment data, consistency between sediments and model simplicity. While transforms can improve the linearity of the relationship between the dependent variable and the model parameters, type I error may also be increased (Personal communication Joan Clarke August 31, 2004). An adequate linear model was therefore preferred.

Preliminary model selection was based on R^2 and p values obtained for the parameters using the Entropy regression. R^2 values for entropy regression tend to be lower than for

conventional regression, however. A definitive R^2 criteria for inclusion in the model was therefore not applied to individual contaminants at this stage of the analysis. The number of compounds for which one or more parameters was not statistically significant were identified. Regression coefficients obtained for the $M_{i\ Predicted} = M_{i\ Measured}$ plots, the R^2 value, the RMSE and the mean difference between predicted and measured values were then collectively examined.

RESULTS

For some compounds, R^2 values were low even though model parameters were statistically significant. This may in part be a consequence of the use of the entropy regression procedure, but was particularly problematic for the New York sediment, for which the linear models produced mostly negative R^2 values. Variance appears to increase with increasing values of the dependent parameter for all three sediments, but most significantly so for the New York sediment. Residuals resulting from regression on the New York sediment exhibit the classic funnel shape indicative of this characteristic.

PAHs. Mean R^2 values for all models are summarized in Table 7-2. The number of parameters produced in the ENTROPY regression that were not statistically significant and the corresponding number of compounds are also given in Table 7-2. Model A was the only model for which all parameter estimates were statistically significant. Although the predictive value of the Model A coefficients for the individual fractions is variable, as can be seen from the plots of predicted to measured contaminant mass (Figures 7-7, 7-8 and 7-9), overall correspondence is relatively good as indicated by the regression coefficient and RMSE.

TABLE 7-2. Mean R^2 Values from ENTROPY Regression for Individual PAHs and Number of Model Parameters with p Values Exceeding 0.05 (Number of Corresponding Compounds in Parenthesis)

Sediment	Model					
	A	B	C	D	BMC	DMC
Calumet	.5197/0	.6101/16 (10)	.6679/0	.6430/32 (16)	.4520/4 (4)	.5229/48 (16)
New Bedford	-0.0464/0	.7502/19 (10)	.6075/16 (15)	.4642/27 (17)	-0.2870/10 (4)	.5450/42 (17)
New York	-0.0877/0	.2529/19 (17)	.7123/3 (3)	.7228/35 (17)	-0.0374/7 (7)	.6883/45 (17)

Phase specific coefficients (equivalent to concentrations) obtained for Model A are given in Tables 7-3, 7-4 and 7-5. With one exception (fluoranthene, New Bedford), highest concentrations were seen in the oil and grease phase for all PAHs, followed by the soot and then organic carbon. Coefficients for oil and grease ranged from 1.5 to 7 times greater than corresponding soot coefficients for Calumet, from 0.7 to 21 times greater for New Bedford, and from 5 to nearly 8 times greater for New York. Oil and grease coefficients ranged from 6.6 to 38 times greater than organic carbon for Calumet, from 2 to 29 times greater for New Bedford, and from 36 to 144 times greater for New York. On a mass basis, the distribution of the total contaminant mass in the sorptive phases for the bulk Calumet sediment was OG 75.6%,

Soot20.5%, OC 3.9%, for New Bedford it was OG 76.8%, Soot 15.5%, OC 7.7%, and for New York it was OG 84.3%, Soot 14.2% and OC 1.5%.

Correspondence of predicted contaminant mass for Model A to the contaminant mass in the bulk sediment generally appears to be good (Tables 7-3, 7-4 and 7-5), but the means are not statistically equal for some compounds. Mean difference between predicted and measured contaminant mass for Calumet was 12.1%, with a minimum of 1.33% and maximum of 38.5%. Mean difference for New Bedford was 6.89%, with a minimum difference of 0.54% and maximum of 18.8%. Mean difference for New York was 11.3%, with a minimum of 1.57% and maximum of 18.7%.

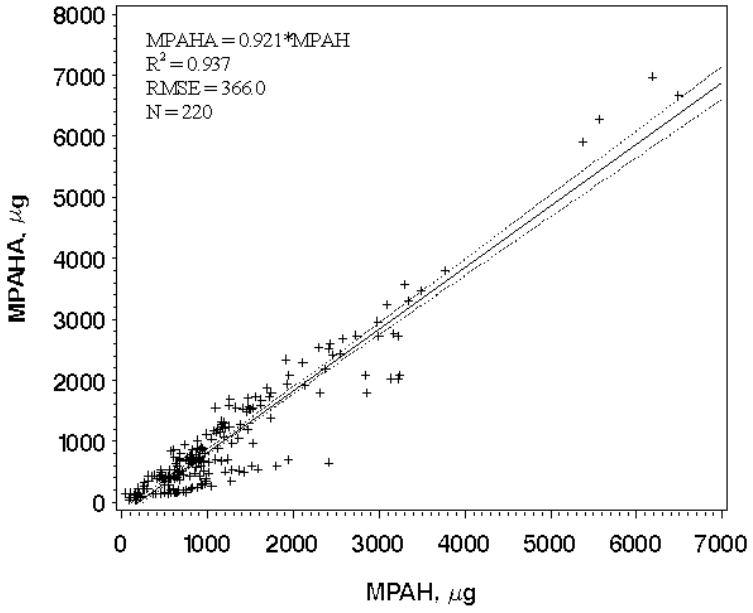

FIGURE 7-7. Calumet Model A mass PAH in sorptive phases as calculated from regression coefficients versus mass measured in corresponding sediment fraction.

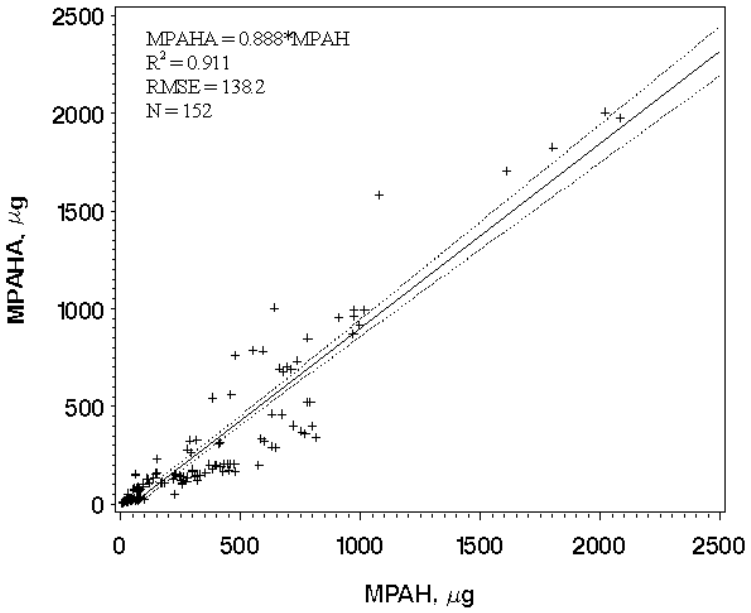

FIGURE 7-8. New Bedford Model A mass PAH in sorptive phases as calculated from regression coefficients versus mass measured in corresponding sediment fraction.

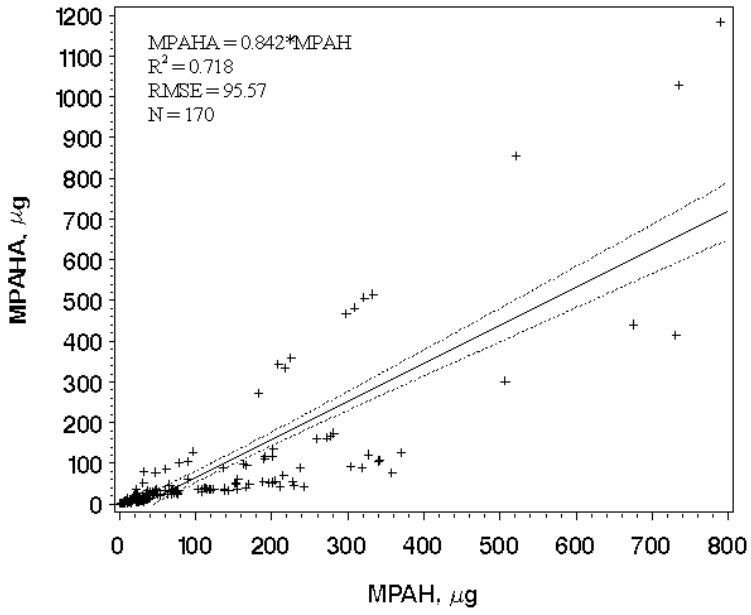

FIGURE 7-9. New York Model A mass PAH in sorptive phases as calculated from regression coefficients versus mass measured in corresponding sediment fraction.

TABLE 7-3. Calumet Model A ENTROPY Regression Coefficients and Mean Predicted Mass of PAH in Sorptive Phases and Bulk Sediment

Compound	Regression Coefficients			R^2	RMSE	Contaminant Mass				
	OG	Soot	OC			OG	Soot	OC	Sum	Bulk
	µg/kg	µg/kg	µg/kg			µg	µg	µg	µg	µg
Acenaphthene	92,587	33,098	6,468	0.5112	152.1	248	370	363	981	801
Acenaphthylene	30,886	11,310	2,326	0.4526	51.7	83	126	131	340	281
Anthracene[a]	188,610	96,095	15,271	0.544	324.8	506	1,074	857	2,436	2,102
Benzo(A)Anthracene[a]	594,002	104,970	16,344	0.7868	406.9	1,592	1,173	917	3,682	3,530
Benzo(A)Pyrene[a]	363,466	116,874	9,596	0.7397	343.2	974	1,306	538	2,819	2,776
Benzo(B)Fluoranthene[a]	338,920	69,989	11,856	0.7388	285.1	909	782	665	2,356	2,325
Benzo(G,H,I)Perylene[a]	145,658	67,068	8,213	0.686	205.0	390	749	461	1,601	1,561
Benzo(K)Fluoranthene	160,081	70,135	11,574	0.6206	265.0	429	784	649	1,862	1,829
Chrysene[a]	516,262	99,489	15,199	0.8486	316.0	1,384	1,112	853	3,348	3,285
Dibenzo(A,H)Anthracene[a]	37,311	25,162	1,416	0.2893	75.6	100	281	79	461	403
Fluoranthene[b]	982,541	189,439	43,023	0.5039	898.7	2,634	2,117	2,414	7,164	6,182
Fluorene	151,434	57,532	10,669	0.5396	252.5	406	643	599	1,647	1,355
Indeno(1,2,3-C,D)Pyrene[a,b]	190,780	64,020	10,246	0.2841	291.6	511	715	575	1,802	1,622
2-Methylnaphthalene[b]	187,775	62,953	7,379	-0.7975	352.4	503	703	414	1,621	1,170
Phenanthrene	365,674	214,510	55,166	0.8676	567.5	980	2,397	3,095	6,472	6,026
Pyrene[b]	839,354	123,717	42,540	0.7006	615.2	2,250	1,382	2,387	6,019	5,374

p value <0.05 for paired t test. H_0: $mean_{pred}$ - $mean_{meas}$ = 0. [a]full data set. [b]bulk sediment data.

TABLE 7-4. New Bedford Model A ENTROPY Regression Coefficients and Mean Predicted Mass of PAH in Sorptive Phases and Bulk Sediment

Compound	Regression Coefficients			R^2	RMSE	Contaminant Mass				
	OG	Soot	OC			OG	Soot	OC	Sum	Bulk
	µg/kg	µg/kg	µg/kg			µg	µg	µg	µg	µg
Acenaphthene	20,024	1,553	785	0.2909	16.7	35.4	1.8	27.0	64.2	67.5
Acenaphthylene[a]	2,272	436	270	0.5398	2.3	4.0	0.5	9.3	13.8	11.7
Anthracene[a]	21,229	5,447	1,164	-3.0654	40.3	37.6	6.4	40.0	84.0	71.1
Benzo(A)Anthracene	352,106	53,766	14,723	-3.4446	292.3	623.1	63.0	506.3	1,192.4	1,003.3
Benzo(A)Pyrene	177,924	54,561	14,920	0.5917	183.5	314.9	63.9	513.0	891.8	981.6
Benzo(B)Fluoranthene[a]	190,320	24,726	17,597	0.5232	172.4	336.8	29.0	605.1	970.9	961.8
Benzo(G,H,I)Perylene[a]	116,740	18,401	13,655	0.4923	123.8	206.6	21.6	469.6	697.7	675.5
Benzo(K)Fluoranthene	113,719	13,676	13,517	0.6215	113.7	201.2	16.0	464.8	682.1	693.2
Chrysene	181,941	24,008	18,228	0.3725	196.9	322.0	28.1	626.8	976.9	971.7
Dibenzo(A,H)Anthracene[b]	27,652	4,278	3,017	0.3511	29.9	48.9	5.0	103.7	157.7	147.5
Fluoranthene[a]	84,185	124,711	42,700	0.8974	166.9	149.0	146.1	1,468.3	1,763.4	1,704.4
Fluorene	26,534	3,184	1,277	0.1002	23.6	47.0	3.7	43.9	94.6	92.8
Indeno(1,2,3-C,D)Pyrene	263,768	12,413	8,942	0.6499	151.6	466.8	14.5	307.5	788.8	756.4
2-Methylnaphthalene[a]	9,054	2,142	1,762	0.804	9.4	16.0	2.5	60.6	79.1	72.5
Naphthalene	13,925	4,036	3,003	0.8591	14.8	24.6	4.7	103.2	132.6	122.3
Phenanthrene	55,901	14,289	4,508	-2.0316	96.6	98.9	16.7	155.0	270.7	284.0
Pyrene	334,595	39,257	39,245	0.6592	329.1	592.1	46.0	1,349.5	1,987.6	2,050.1

p value <0.05 for paired t test. H_0: $mean_{pred}$ - $mean_{meas}$ = 0. [a]full data set. [b]bulk sediment data.

TABLE 7-5. New York Model A ENTROPY Regression Coefficients and Mean Predicted Mass of PAH in Sorptive Phases and Bulk Sediment

Compound	Regression Coefficients					Contaminant Mass				
	OG µg/kg	Soot µg/kg	OC µg/kg	R^2	RMSE	OG µg	Soot µg	OC µg	Sum µg	Bulk µg
Acenaphthene	11,383	2,248	94	-0.4648	9.7	13.7	8.0	1.8	23.4	20.3
Acenaphthylene	4,464	833	31	0.2475	2.6	5.4	3.0	0.6	8.9	8.0
Anthracene	85,880	14,838	1,436	0.475	42.9	103.5	52.5	27.0	183.1	175.1
Benzo(A)Anthracene	160,279	26,405	1,810	-0.2227	109.6	193.2	93.5	34.1	320.8	284.2
Benzo(A)Pyrene	170,140	28,202	2,079	-0.2211	112.8	205.1	99.9	39.2	344.1	307.2
Benzo(B)Fluoranthene	148,173	26,437	2,239	-0.1279	94.7	178.6	93.6	42.2	314.4	285.0
Benzo(G,H,I)Perylene	106,696	18,797	1,587	-0.0881	66.8	128.6	66.6	29.9	225.1	204.2
Benzo(K)Fluoranthene	106,524	20,276	1,571	-0.5621	78.7	128.4	71.8	29.6	229.8	204.8
Chrysene	164,496	29,110	1,851	-0.3482	115.5	198.3	103.1	34.9	336.3	299.1
Dibenzo(A,H)Anthracene	22,740	4,192	623	-0.7165	18.4	27.4	14.8	11.7	54.0	45.5
Fluoranthene	272,477	46,872	4,459	-0.3704	191.1	328.5	166.0	84.0	578.4	513.8
Fluorene	15,954	2,945	227	-0.4965	11.8	19.2	10.4	4.3	33.9	29.5
Indeno(1,2,3-C,D)Pyrene	108,907	18,969	2,565	-0.3674	77.8	131.3	67.2	48.3	246.8	213.4
2-Methylnaphthalene	25,424	4,615	672	0.3595	13.8	30.7	16.3	12.7	59.6	54.9
Naphthalene	40,632	6,683	769	0.5734	17.3	49.0	23.7	14.5	87.1	81.1
Phenanthrene	333,606	43,831	8,672	0.716	141.8	402.2	155.2	163.3	720.7	732.2
Pyrene	356,563	65,184	8,008	0.1229	212.1	429.9	230.8	150.8	811.5	732.2

There were no compounds for which p value <0.05 for paired t test. H_0: $mean_{pred} - mean_{meas} = 0$.

PCBs. Mean R^2 values for PCBs modeled are summarized in Table 7-6. Each model returned some parameter estimates that were not statistically significant. The number of these for each model and the corresponding number of compounds are also given in Table 7-6. For Calumet and New Bedford, Models A and BMC returned the greatest number of statistically significant parameters. For New York, Models A and D produced the greatest number of significant parameters. An F test on SSE/MSE indicates R^2 values of Models A and BMC are statistically different for 24 of 25 PCBs for Calumet and 8 of 43 PCBs for New Bedford. For a number of these compounds, however, one or more parameters were not statistically significant for Model BMC. Although predicted to measured PCBs are not as highly correlated for Model A overall (Figures 7-10, 7-11 and 7-12) Model A was selected as the best fit model based largely on the statistical significance of the parameter estimates.

TABLE 7-6. Mean R^2 Resulting from ENTROPY Regression for PCBs and Number of Model Parameters with p Values Exceeding 0.05 (Number of Corresponding Compounds in Parenthesis)

Sediment	Model					
	A	B	C	D	BMC	DMC
Calumet	.5202/7 (7)	.7760/46 (31)	.3805/20 (15)	-1.226/76 (35)	.8153/18 (12)	.0442/101 (45)
New Bedford	.7312/6 (2)	.6948/23 (13)	.6079/45 (43)	.4856/67 (43)	.7526/6 (2)	.5050/96 (43)
New York	-.3186/13 (5)	.1155/57 (26)	.3995/11 (7)	.3724/84 (34)	-.2938/72 (34)	.3118/95 (34)

Phase specific coefficients obtained from the ENTROPY regression for Model A and corresponding contaminant mass are given in Tables 7-7, 7-8 and 7-9. For Calumet, with the exception of PCBs 86 and 97, highest concentrations were seen in the oil and grease phase. Except for PCBs 18, 52, 70 and 208, concentrations in soot were also higher than organic carbon. Coefficients for oil and grease ranged from approximately ½ of the soot coefficient to 17 times greater, with a mean coefficient ratio of 6.7, and from approximately ½ of the OC coefficient to 43 times greater, with a mean coefficient ratio of 13.6. For New Bedford, coefficients for oil and grease ranged from approximately 7 to 63 times greater than soot, and 12 to 33 times greater than OC with mean ratios of 28 and 17 respectively. For New York, coefficients for oil and grease ranged from 3 to 5 times that of soot, with a mean ratio of 4 and from 4 to 73 times greater than OC, with a mean ratio of 34. As for PAHs, correspondence to bulk sediment contaminant mass is relatively good (Tables 7-7, 7-8 and 7-9). The distribution of the total contaminant mass in the sorptive phases for the bulk Calumet sediment is as follows: OG 25.6%, Soot 16.6% and OC 57.8%. For New Bedford, contaminant mass distribution is: OG 42.5%, Soot 0.7% and OC 56.8%. For New York, contaminant mass distribution is: OG 42.4%, Soot 27.9% and OC 29.7%.

DISCUSSION

With one exception (New Bedford, Flouranthene), oil and grease was the preferred phase for PAHs for all three sediments. The distribution between soot and OC was more variable, with some compounds reporting almost equally to soot and OC fractions in New Bedford, and the remainder distributing to the soot over the OC. The distinction between the soot and OC

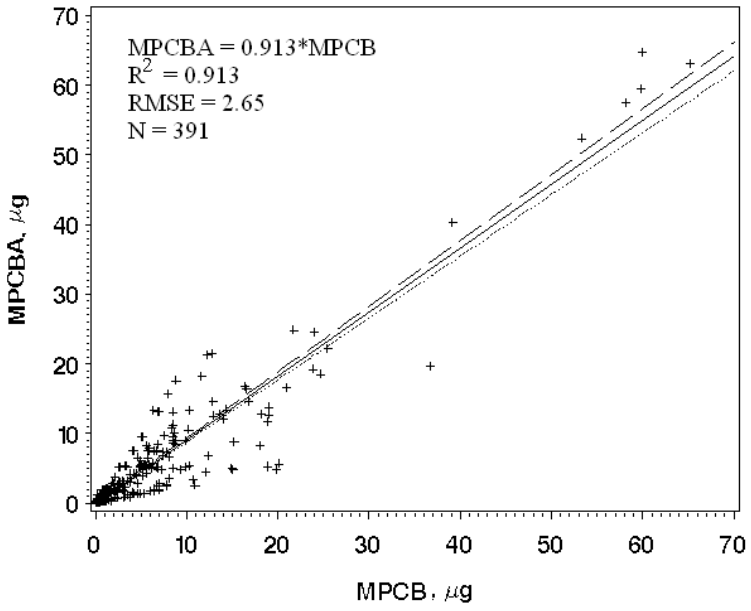

FIGURE 7-10. Calumet Model A mass PCB in sorptive phases as calculated from regression coefficients versus mass measured in corresponding sediment fraction.

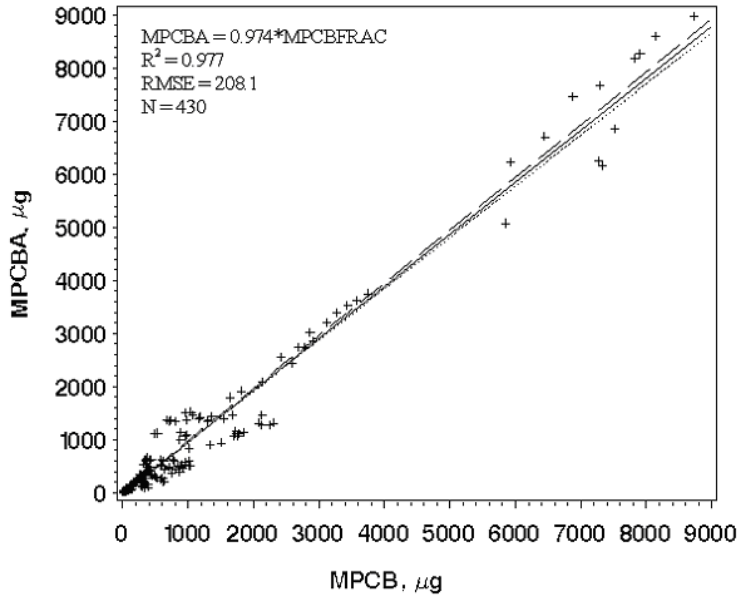

FIGURE 7-11. New Bedford Model A mass PCB in sorptive phases as calculated from regression coefficients versus mass measured in corresponding sediment fraction.

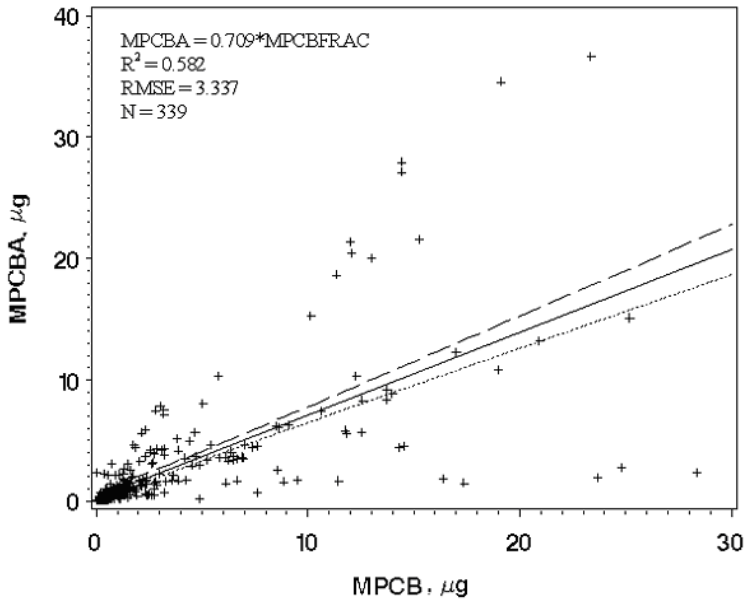

FIGURE 7-12. New York Model B mass PCB in sorptive phases as calculated from regression coefficients versus mass measured in corresponding sediment fraction.

fractions was relatively clear for Calumet and New York, where the concentration of all PAHs was higher in the soot than in the OC (Figure 7-13). Differences with respect to contaminant distribution between soot and OC are likely due to the relative aromaticity of both phases, the surface area of the soot fraction and the planarity of the compounds. Aliphatic organic matter appears to have a lower affinity for hydrophobic organic contaminants than aromatic organic matter (Hwang and Cutright 2004; Chiou, McGroddy and Kile 1998). While condensed phases such as the coal fragments seen in Calumet likely have high affinity for organic contaminants, specific surface area is expected to be relatively low due to the coarse particle size (Bucheli and Gustafsson 2000). The soot phase in New York could not readily be visualized, suggesting that it is very fine with a high surface area. These observations are consistent with the observed contaminant distribution as determined by regression.

With only three exceptions, oil and grease was also the preferred phase for PCBs for all three sediments. As for PAHs, PCB concentration in soot was equal to or higher than in OC for Calumet (except for PCBs 18, 52, 70 and 208). There was a marked difference for all PCBs between soot and OC phases for New York, but almost comparable concentrations for all PCBs for New Bedford. This may be a reflection of a finer, more aromatic soot fraction in New York or a more aromatic OC fraction in Calumet and New Bedford. Although non-planar PCBs have been observed to have a reduced affinity for soot due to steric effects (Cornelissen et al. 2004a), no consistent trends were identified to explain the differences in soot affinity for PCBs in the study sediments.

There is some indication that clay minerals also play a role in PCB sorption, as evidenced by the correlation to the mineral clay fraction obtained for a number of the PCBs in Calumet and New Bedford. Regression coefficients obtained for the clay phase suggest concentrations much lower than for any of the other phases, however. Ghosh, Zimmerman and Luthy (2003) reported higher concentrations of PAHs and PCBs to high density (non-carbonaceous) phases in the fine fraction of three natural sediments, which they attributed to high surface area and relative abundance of mineral phases in this size fraction. Hwang and Cutright (2004) reported higher sorption of PAHs to soils containing vermiculite and kaolinite than to the aliphatic organic matter in the soils. They attributed this to high external surface area of the clays present and, for the vermiculate, internal surface areas as high as 570-700 m^2/g. Cornelissen et al. (2004a) reported nanopore surface area for soot in Lake Ketelmeer sediments in the range of 58 m^2/g. Based on relative surface areas, some clay materials could be a competitive phase relative to soot even for hydrophobic organic contaminants.

SUMMARY AND CONCLUSIONS

Initial efforts to obtain correlations between contaminant concentration or mass and the sorptive phases using the fractionation data were unsuccessful. Negative coefficients, which were not physically meaningful, usually resulted for one or more of the regression variables. Stepwise regression and data transforms were not effective in producing a model including all of the measured sorptive phases. In part, these problems were likely a result of collinearity in the data set, and in one case, instability of variance. An entropy based regression procedure designed for ill-conditioned data was successful in producing consistent results for regression of measured PAH mass against the linear combination of the mass of the sorptive phases. Regression coefficients obtained represent the contaminant concentration associated with each of

TABLE 7-7. Calumet Model A ENTROPY Regression Coefficients and Mean Predicted Mass of PCB in Sorptive Phases and Bulk Sediment

Compound	Regression Coefficients			R^2	RMSE	Contaminant Mass				
	OG	Soot	OC			OG	Soot	OC	Sum	Bulk
	µg/kg	µg/kg	µg/kg			µg	µg	µg	µg	µg
PCB101	1581.4	741.5	363.7	-0.6893	4.98	4.45	8.69	21.4	34.6	40.6
PCB114	137.4	26.8	15.9	0.5755	0.30	0.386	0.314	0.936	1.64	1.54
PCB118	600.1	486.3	290.0	-0.6291	3.59	1.69	5.70	17.1	24.5	30.7
PCB128	797.9	83.4	41.1	0.8871	0.60	2.24	0.977	2.42	5.64	6.01
PCB136	355.2	77.1	32.1	0.3636	1.08	1.00	0.904	1.89	3.79	3.64
PCB138	492.5	401.2	222.4	-0.808	3.04	1.39	4.70	13.1	19.2	26.8
PCB141	661.0	91.0	45.1	0.8532	0.70	1.86	1.07	2.66	5.58	5.87
PCB151	942.5	94.1	46.7	0.8763	0.74	2.65	1.10	2.75	6.51	6.87
PCB156	299.9	37.1	26.4	0.9027	0.27	0.844	0.435	1.55	2.83	2.97
PCB170	362.1	40.6	18.9	0.7172	0.35	1.02	0.476	1.11	2.61	2.50
PCB18	7642.6	539.5	539.3	0.9026	5.30	21.50	6.33	31.8	59.6	57.8
PCB180	622.8	71.6	45.7	0.8921	0.47	1.75	0.840	2.69	5.28	5.21
PCB183	187.4	23.6	9.2	0.7425	0.17	0.527	0.277	0.54	1.35	1.30
PCB189	29.1	4.7	1.0	0.39	0.05	0.082	0.055	0.059	0.196	0.20
PCB194	104.6	20.1	11.2	0.7656	0.15	0.294	0.236	0.659	1.19	1.13
PCB195	54.6	7.5	1.9	0.6073	0.06	0.154	0.087	0.111	0.352	0.334
PCB196	117.1	11.2	4.4	0.8298	0.10	0.329	0.131	0.259	0.720	0.768
PCB199	32.6	4.4	3.2	0.8685	0.03	0.092	0.052	0.186	0.330	0.334
PCB201	88.1	28.3	8.5	0.3851	0.21	0.248	0.332	0.500	1.08	0.968
PCB203	177.4	24.5	8.6	0.7501	0.22	0.499	0.287	0.507	1.29	1.33
PCB206[a]	45.8	22.3	4.3	0.6603	0.08	0.129	0.261	0.251	0.641	0.601
PCB208	73.4	6.0	8.0	0.9239	0.08	0.206	0.070	0.472	0.748	0.801
PCB28	7150.7	1046.4	534.4	0.6984	9.54	20.1	12.3	31.5	63.9	62.6
PCB40	1014.8	121.4	80.0	0.7524	1.05	2.85	1.42	4.71	8.99	8.48
PCB44	4690.1	556.6	354.5	0.777	4.79	13.19	6.53	20.9	40.6	45.3
PCB49	982.7	608.7	429.4	0.1149	4.01	2.76	7.14	25.3	35.18	38.19
PCB52	7263.9	487.0	532.3	0.8728	6.01	20.4	5.71	31.3	57.5	56.9
PCB54	43.1	12.9	1.0	0.4386	0.09	0.121	0.152	0.059	0.332	0.334
PCB66	1574.0	523.4	496.4	0.629	2.55	4.43	6.14	29.2	39.8	13.8
PCB7	204.8	30.7	13.9	0.8265	0.27	0.576	0.360	0.820	1.76	2.00
PCB70	7081.5	412.3	469.2	0.9002	4.86	19.9	4.83	27.6	52.4	50.4
PCB8	1978.6	355.7	252.9	0.617	3.86	5.57	4.17	14.9	24.6	22.8
PCB86	102.3	250.8	170.1	-0.4921	2.04	0.29	2.94	10.0	13.2	4.80
PCB87	2265.0	249.7	123.7	0.7974	2.07	6.37	2.93	7.28	16.6	16.5
PCB97	102.3	250.8	170.1	-0.4921	2.04	0.288	2.94	10.0	13.2	4.80

p value <0.05 for paired t test. H_0: $mean_{pred}$ - $mean_{meas}$ = 0. [a]full data set. [b]bulk sediment data.

TABLE 7-8. New Bedford Model A ENTROPY Regression Coefficients and Mean Predicted Mass of PCB in Sorptive Phases and Bulk Sediment

Compound	Regression Coefficients			R^2	RMSE	Contaminant Concentration				
	OG µg/kg	Soot µg/kg	OC µg/kg			OG µg	Soot µg	OC µg	Sum µg	Bulk µg
PCB1	4,881.4	388.5	245.5	-0.235	15.57	8.64	0.455	8.44	17.5	0.336
PCB101	826,717.9	19,488.7	58,429.9	0.9477	263.83	1,463	22.8	2,009	3,495	3,416
PCB103	44,995.8	808.3	899.7	0.8867	13.86	79.6	0.947	30.9	112	121
PCB114	11,874.0	571.5	782.5	0.8234	6.57	21.0	0.670	26.9	48.6	42.5
PCB118	636,829.3	23,977.7	43,188.0	0.9191	236.64	1,127	28.1	1,485	2,640	2,547
PCB126[a]	3,476.8	358.8	231.2	0.6391	2.25	6.15	0.421	7.95	14.5	13.8
PCB128	30,450.2	1,853.5	2,297.0	0.7637	20.81	53.9	2.17	78.98	135	115
PCB136	96,763.6	4,462.1	6,888.1	0.8301	54.95	171	5.23	237	413	365
PCB137	22,215.8	895.9	1,153.2	0.8979	8.40	39.3	1.05	39.7	80.0	72.1
PCB138	243,027.5	15,358.2	16,948.7	0.7996	139.24	430	18.0	583	1,031	912
PCB141	37,375.6	570.4	2,114.9	0.9722	7.90	66.1	0.668	72.7	140	141
PCB151	129,494.4	3,049.1	4,707.0	0.9115	38.06	229	3.57	162	395	374
PCB156	43,711.6	1,386.1	1,554.2	0.8585	15.75	77.4	1.62	53.4	132	120
PCB167	31,456.5	1,177.3	1,810.0	0.9231	10.59	55.7	1.38	62.2	119	112
PCB170	36,143.5	1,486.1	1,844.7	0.8805	13.74	64.0	1.74	63.4	129	120
PCB18	1,589,100.7	30,440.5	105,092.5	0.9542	498.81	2,812	35.7	3,614	6,461	6,187
PCB180	54,456.1	3,069.5	3,345.9	0.9037	20.56	96.4	3.60	115	215	200
PCB183	16,885.8	1,110.8	1,241.3	0.779	10.78	29.9	1.30	42.7	73.9	63.6
PCB185	4,238.8	264.9	243.5	0.7546	2.48	7.50	0.310	8.37	16.2	13.8
PCB189	2,517.4	79.4	188.7	0.9539	0.78	4.45	0.093	6.49	11.0	11.2
PCB191	2,438.8	53.9	112.9	0.8309	1.27	4.32	0.063	3.88	8.26	9.50
PCB194	6,843.5	370.0	466.5	0.6853	4.80	12.1	0.434	16.0	28.6	30.2
PCB195[a]	3,239.6	333.8	233.8	0.4528	2.68	5.73	0.391	8.04	14.2	12.6
PCB196	3,886.9	266.4	243.6	0.7316	2.29	6.88	0.312	8.38	15.6	14.4
PCB199	2,236.1	117.6	128.2	0.8157	1.14	3.96	0.138	4.41	8.50	7.51
PCB201	6,502.8	457.1	473.0	0.8393	3.33	11.5	0.536	16.3	28.3	26.4
PCB202	2,465.5	163.1	157.5	0.6185	1.98	4.36	0.191	5.42	9.97	8.02
PCB203	4,661.6	640.5	301.4	0.2963	4.14	8.25	0.751	10.4	19.4	16.1
PCB206[a]	5,715.4	315.8	212.3	0.8459	2.04	10.1	0.370	7.30	17.8	17.2
PCB207	1,508.7	58.6	45.3	0.8718	0.49	2.67	0.069	1.56	4.30	3.89
PCB208	2,163.4	114.5	93.1	0.708	1.18	3.83	0.134	3.20	7.16	7.45
PCB28	1,832,276.8	35,773.2	159,893.4	0.9598	603.66	3,242	41.92	5,498	8,782	8,433
PCB40	81,094.4	3,386.6	6,079.5	0.8609	43.31	144	3.97	209	357	319
PCB44	702,737.4	15,519.3	53,575.4	0.9406	253.73	1,244	18.2	1,842	3,104	2,989
PCB49	2,112,030.3	33,989.4	117,396.3	0.9446	652.29	3,737	39.8	4,037	7,814	7,352
PCB52	1,970,863.9	34,091.2	129,140.7	0.9559	598.02	3,488	40.0	4,441	7,968	7,592
PCB66	318,305.2	28,240.8	23,506.2	0.2771	370.96	563	33.1	808	1,405	1,024
PCB7	8,692.8	909.2	407.2	-0.8144	27.10	15.4	1.07	14.0	30.5	1.48
PCB70	430,125.0	16,455.3	31,070.0	0.9072	180.64	761	19.3	1,068	1,849	1,719
PCB8	826,441.9	14,770.5	62,786.2	0.9601	251.63	1,462	17.3	2,159	3,639	3,583
PCB82	17,954.2	635.2	1,461.7	0.9063	8.21	31.8	0.744	50.3	82.8	77.6
PCB87	51,608.3	3,016.9	4,474.3	0.8559	28.44	91.3	3.54	154	249	232
PCB97	154,161.5	13,799.9	9,914.3	-0.1731	253.93	273	16.2	341	630	361

p value <0.05 for paired t test. H_0: $mean_{pred}$ - $mean_{meas}$ = 0. [a]full data set. [b]bulk sediment data.

TABLE 7-9. New York Model A ENTROPY Regression Coefficients and Mean Predicted Mass of PCB in Sorptive Phases and Bulk Sediment

Compound	Sorptive Phase			R^2	RMSE	Contaminant Mass				
	OG µg/kg	Soot µg/kg	OC µg/kg			OG µg	Soot µg	OC µg	Sum µg	Bulk µg
PCB101	5,161.4	1,121.5	234.9	-0.1003	4.61	6.22	3.97	4.42	14.6	13.0
PCB118	4,614.7	1,006.2	229.5	0.0079	3.83	5.56	3.56	4.32	13.4	11.9
PCB128	609.7	145.1	29.1	-0.0381	0.48	0.735	0.514	0.549	1.80	1.58
PCB138	3,422.8	785.2	234.7	0.3163	2.62	4.13	2.78	4.42	11.3	10.4
PCB141	745.7	162.9	51.6	0.1066	0.58	0.899	0.577	0.972	2.45	2.15
PCB151	1,140.9	334.8	59.4	0.5083	0.75	1.38	1.19	1.12	3.68	3.39
PCB156	404.3	101.7	26.5	0.4395	0.28	0.487	0.360	0.498	1.35	1.23
PCB167	220.5	50.1	7.4	-0.6874	0.22	0.266	0.178	0.139	0.582	0.495
PCB170	871.9	200.4	48.8	0.1027	0.66	1.05	0.710	0.918	2.68	2.35
PCB18	5,830.9	1,267.1	176.8	-0.2354	6.37	7.03	4.49	3.33	14.8	12.8
PCB180	1,856.6	501.5	88.3	0.0334	1.49	2.24	1.78	1.66	5.68	5.12
PCB183	539.7	130.9	23.9	-0.3431	0.46	0.651	0.464	0.450	1.56	1.36
PCB185	175.6	42.0	3.6	-3.6799	0.23	0.212	0.149	0.068	0.428	0.275
PCB189	114.4	32.0	3.3	-0.5997	0.09	0.138	0.113	0.062	0.314	0.257
PCB194	610.2	148.5	9.5	-0.4513	0.75	0.736	0.526	0.179	1.44	1.19
PCB195	431.4	94.7	21.5	0.7059	0.24	0.520	0.335	0.406	1.26	1.28
PCB196	396.6	97.0	6.8	-0.5579	0.48	0.478	0.344	0.127	0.949	0.771
PCB199	120.3	32.3	2.4	-0.6168	0.16	0.145	0.115	0.046	0.305	0.239
PCB201	863.7	210.6	13.4	-0.4203	1.02	1.04	0.746	0.253	2.04	1.71
PCB202	163.4	44.6	4.3	-1.0945	0.23	0.197	0.158	0.082	0.437	0.349
PCB203	738.1	181.3	12.4	-0.3356	0.82	0.890	0.642	0.233	1.76	1.52
PCB206	600.9	147.4	8.4	-0.5565	0.85	0.724	0.522	0.158	1.40	1.10
PCB207	75.1	18.5	1.0	-0.7429	0.12	0.091	0.065	0.019	0.175	0.128
PCB208	284.7	66.8	4.7	-1.2649	0.39	0.343	0.236	0.089	0.669	0.514
PCB28	9,497.8	2,084.3	266.4	-0.3798	10.52	11.5	7.38	5.02	23.8	20.0
PCB40	804.0	215.4	155.2	0.87	0.58	0.969	0.763	2.92	4.66	4.68
PCB44	4,816.4	1,069.1	263.6	0.2715	3.87	5.81	3.79	4.96	14.6	13.3
PCB49	7,388.7	1,546.9	242.0	-0.251	8.62	8.91	5.48	4.56	18.9	16.7
PCB52	9,507.2	2,125.3	365.4	0.1434	9.08	11.5	7.53	6.88	25.9	24.3
PCB66	7,573.5	1,781.6	195.2	-2.0011	8.17	9.13	6.31	3.68	19.1	13.3
PCB70	4,254.0	893.0	457.4	0.6003	3.33	5.13	3.16	8.61	16.9	16.1
PCB8	2,845.1	601.7	85.8	-0.2481	3.02	3.43	2.13	1.62	7.18	6.07
PCB82	684.6	129.7	156.6	0.9519	0.32	0.825	0.459	2.95	4.23	4.29
PCB97	876.2	199.6	13.6	-1.2865	1.98	1.06	0.707	0.256	2.02	0.62

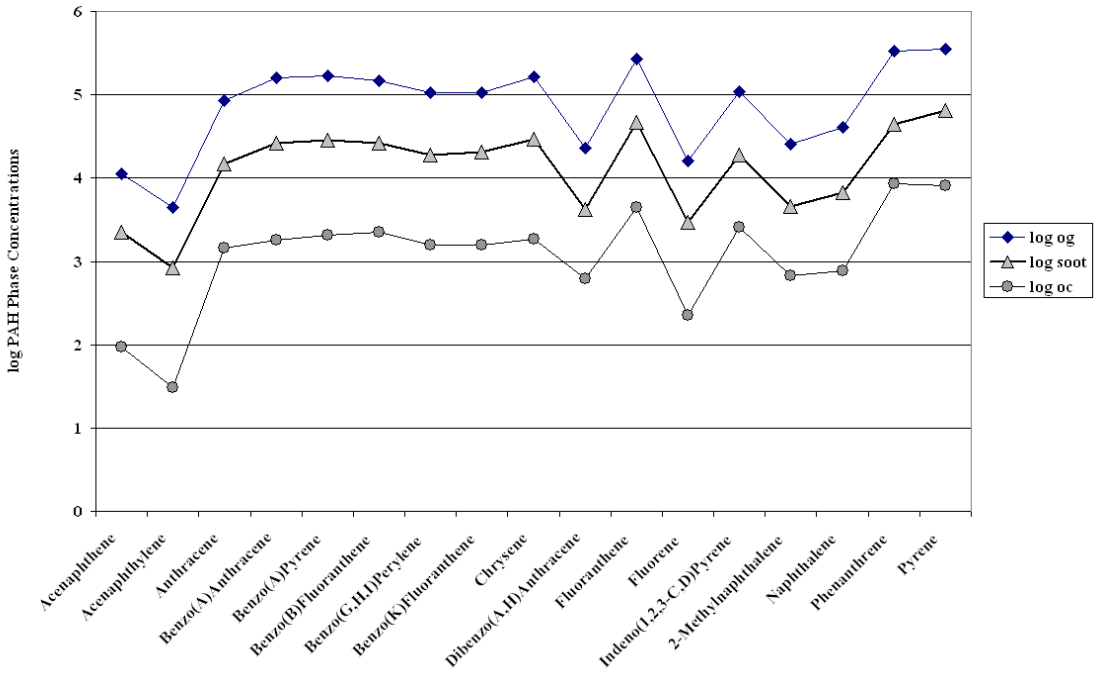

FIGURE 7-13. New York sediment, relative PAH concentration in sorptive phases.

the sorptive phases in the model. The sum of the predicted contaminant mass in the sorptive phases corresponded more closely to measured values for bulk sediment than for fractions. This was thought to occur because the bulk sediment concentrations represent a central value, with concentrations in the size and density fractions being generally much higher or lower than the bulk sediment.

Based on results of the entropy regression, oil and grease is the least abundant sorptive phase for all three sediments, yet contains contaminant mass approximately equal to, or greater than, OC or soot for a number of PCBs and PAHs. For New York, oil and grease was the most important phase for all but 5 PCBs and all PAHs, though the mean mass ratio of OG/OC was less than 6%. Similarly, soot was a more important phase for PAHs in New York than organic carbon, in spite of a mean Soot/OC mass ratio of only 22%. Conversely, contaminant mass was distributed more evenly between all three phases in Calumet, even with a relatively high proportion of soot to OC (mean 78%). In New Bedford, with a mean Soot/OC ratio of 3.4%, soot contained the lowest contaminant mass for all PAHs and PCBs in New Bedford. Low contaminant mass in an abundant sorptive phase (Calumet soot), relative to that observed for other sediments (New York soot) suggests significant differences in the composition of the soot and OC phases between sediments. The predicted contaminant distribution obtained by regression appears to reflect these differences and appears to be consistent with the observed character of the sediments. Contaminant concentrations attributed to the different sorptive phases are therefore considered to be reasonable, and a suitable basis for estimation of phase specific distribution coefficients for the bulk sediment.

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CHAPTER 8

PHASE SPECIFIC DISTRIBUTION COEFFICIENTS – PART 1: PAHS

INTRODUCTION

Conventional methods of deriving distribution coefficients, whether theoretical or site-specific, provide little information regarding the relative contaminant loading of each of the sorptive phases (Hansen et al. 1999; EPA 1999; Girvin and Scott 1997). Distribution coefficients may be normalized to organic carbon, but organic carbon itself may be composed of several different phases, each with different properties (Cornelissen et al. 2004a and b; Hwang and Cutright 2004). Oil and grease, soot and organic carbon all comprise a portion of the total organic carbon (TOC) measurement, yet partitioning to these phases and bioavailability may be vastly different (Jonker et al. 2003). The ultimate disposition of each of these phases as a consequence of treatment may also be different and may determine the effectiveness of treatment (Olin-Estes et al. 2002). Direct measurement of phase specific contaminant concentrations, however, is not practical due to the difficulty of separating the sorptive phases in quantities sufficient for analysis and without destroying the compounds of interest. Fractionation studies were conducted on three natural sediments in order to obtain differential measurements of PAHs, PCBs, and sorptive phases. Data obtained from these studies was used to establish correlations between contaminant mass and mass of the sorptive phases (Chapter 7). The resulting model was used to develop phase specific distribution coefficients. Results obtained were compared to the observed distribution coefficients for these sediments, as well as theoretical and organic carbon normalized values, and values reported in the literature for partitioning to oil and grease, soot and TOC. Results obtained for PAHs are reported in this chapter; PCBs will be reported in Chapter 9.

METHODS

Fractionation Studies and Correlations. Fractionation studies were conducted on three natural sediments, obtained from Calumet River, New York Harbor and New Bedford Harbor. The sediments were homogenized and then separated into three operationally defined size fractions and two density fractions (Chapters 5 and 6). Contaminant concentrations and concentration of sorptive phases were measured in each fraction and in the bulk sediment. The data was then analyzed to establish statistical correlations between contaminant distribution and the sorptive phases (Chapter 7). A linear model was obtained expressing the distribution of the contaminant mass with respect to the sorptive phases:

$$M_i = C_{i_{OG}} * M_{OG} + C_{i_{Soot}} * M_{Soot} + C_{i_{OC}} * M_{OC} \quad (8\text{-}1)$$

where

M_i = mass of contaminant i in the bulk sediment or operationally defined fraction (μg/kg)

C_{iOG}, C_{iSoot} and C_{iOC} = concentration of contaminant i in the oil and grease (OG), soot and organic carbon (OC) phases (μg/kg)

M_{OG}, M_{Soot} and M_{OC} = mass of the sorptive phases in the bulk sediment and operationally defined size and density fractions (kg)

Visual Phase Identification. Small samples of each sediment were washed through sieves to separate the 250 - 500 μm particles and the 500 μm - 4.75 mm particles. These fractions were then dried and placed in pietre dishes for examination.

Corrections to Pore Water Concentrations. Raw data obtained from analyses of sediment and pore water in the fractionation studies were reported in Chapters 5 and 6. Pore water concentrations were adjusted here for losses occurring during processing and for DOC associated contaminants. The adjusted values were used for calculation of distribution coefficients. The magnitude of sorption losses to Nalgene centrifuge containers was determined by making up PAH and PCB solutions from standards at concentrations comparable to the pore water. Half of the solution was placed in glass jars and half in Nalgene centrifuge bottles. Samples in the centrifuge bottles were centrifuged for a period of time comparable to that required to recover pore water from the sediments. Centrifuged and un-centrifuged samples were then analyzed at the same time and contaminant loss calculated based on concentration differences.

Corrections to pore water concentrations for DOC associated contaminants initially utilized an organic carbon normalized distribution coefficient based on the theoretical distribution coefficient (K_D), based on bulk sediment properties and obtained using (DiToro et al. 1991):

$$K_D = \frac{0.617 * f_{OC} * K_{OW}}{1 + \left(0.617 \times 10^{-6} DOC * K_{OW}\right)} \tag{8-2}$$

where

f_{OC} = fraction organic carbon in the solids (TOC(%)/100)
K_{OW} = octanol-water equilibrium partitioning coefficient (unitless)
DOC = dissolved organic carbon concentration in porewater (mg/L)

The (theoretical) organic carbon normalized distribution coefficient is given as:

$$K_{oc} = K_D / f_{oc} \tag{8-3}$$

where

K_{oc} = ratio of the contaminant concentration on the organic matter on a dry weight basis to dissolved concentration in the surrounding fluid (L/kg)

The theoretical contaminant concentration associated with the DOC, is then:

$$C_{i_{OC}} = K_{OC} * C_{i_{PW}} \tag{8-4}$$

$C_{i,PW}$ = measured contaminant concentration in pore water (μg/L)

The DOC associated contaminants are subtracted from the measured concentration to obtain the DOC corrected pore water concentration. In this case negative pore water concentrations resulted for a number of compounds. A site-specific estimate of contaminant concentration associated with DOC is also available, however, in the form of the regression coefficient obtained for organic carbon from statistical analysis of the fractionation data. This value was used to adjust the pore water concentrations for DOC and produced positive pore water concentrations for most compounds. This pore water concentration was therefore used for calculation of the observed and phase specific distribution coefficients for all sediments.

Observed Distribution Coefficient. The observed distribution coefficient is given as:

$$K_{D_{OBS}} = C_{i_{Bulk}} / C_{i_{PWC}} \tag{8-5}$$

where

C_{iBulk} = concentration of contaminant i in the bulk sediment (μg/kg)
C_{iPWC} = concentration of contaminant i in the pore water, corrected for sorption losses and DOC (using the model specific organic carbon concentration) (μg/L)

Phase Specific Distribution Coefficients. Distribution coefficients were obtained for oil and grease, soot and organic carbon using the phase specific contaminant concentrations determined previously by regression of the fractionation data (Chapter 7) and the DOC adjusted pore water concentration. Two cases were used in calculating the phase specific distribution coefficients: 1) each phase was assumed to be in equilibrium with the pore water at the measured concentration (uniform pore water assumption), and 2) the dissolved concentration was assumed to be largely attributable to the labile phases (nonuniform pore water assumption). Case 2 implies that the labile phases are in equilibrium with the pore water while the non-labile phase is not in equilibrium with the pore water (slow sorption to this phase is occurring).

If each phase is assumed to be in equilibrium with the pore water, the following equality must be satisfied:

$$\frac{C_{i_{OG}}}{K_{D_{OG}}} = \frac{C_{i_{Soot}}}{K_{D_{Soot}}} = \frac{C_{i_{OC}}}{K_{D_{OC}}} \tag{8-6}$$

Equation 8-6 derives from the following equation, where $C_{i,PW}$ is the same value for each equality:

$$K_{D_{OG}} = \frac{C_{i_{OG}}}{C_{i_{PW}}}, \quad K_{D_{Soot}} = \frac{C_{i_{Soot}}}{C_{i_{PW}}}, \quad and\ K_{D_{OC}} = \frac{C_{i_{OC}}}{C_{i_{PW}}} \tag{8-7}$$

Algebraically, pore water concentrations at which Equation 8-6 is satisfied include: 1) the measured pore water concentration and 2) the measured pore water concentration/number of equalities (or phases). Condition 1 constitutes the uniform pore water assumption. Arbitrary division of the pore water concentration between the phases, as required for condition 2, was not thought to be physically meaningful, however. Rather, for the nonuniform pore water assumption, the measured pore water concentration was used for calculation of the distribution coefficients for the labile phases. The equilibrium pore water concentration for the desorption resistant fraction was calculated as described in the following section.

Nonuniform Pore Water Assumption. For the nonuniform pore water assumption, the approximate equilibrium pore water concentration for the respective phases was estimated based on the desorption-resistant and labile behavior of the contaminants. The desorption-resistant and labile contaminant concentrations in the bulk sediment were determined with infinite sink testing similar to that described in Pignatello (1990). Wet sediment was mixed with a sorbent (XAD2-Amberlite) at a ratio of approximately 10% XAD per unit weight dry sediment. The XAD was first activated by washing with methanol, shaking the mixture for 30 minutes, and then washing with DDI three to four times to remove the methanol. Sediment and XAD were then stirred together gently and allowed to sit in an incubator at 25ºC for approximately 24 hours. $ZnCl_2$ solution at a density of approximately 1.1 g/cm^3 was then stirred into the sediment/sorbent mixture. The slurry was stirred gently and the rising XAD pipetted from the surface onto a 100 µm sieve. Fluids and particles passing the sieve were added back to the sediment slurry. After all of the visible XAD was removed from the slurry, the slurry was centrifuged and the $ZnCl_2$ solution decanted. The sediment was washed with DDI, centrifuged and decanted twice more to remove any remaining $ZnCl_2$. The XAD was dried at room temperature. Light debris reporting with the XAD was removed manually and placed back in the sediment. Bulk sediment contaminants were measured in triplicate, before and after the desorption procedure. Contaminant remaining in the sediment after desorption was considered to be desorption-resistant. Contaminant sorbing to the XAD was considered to be labile.

The next step was to estimate the equilibrium pore water concentration that would be expected if the desorption-resistant fraction were allowed to equilibrate with the pore water in the absence of the labile phases. This was obtained by first calculating the K_{OC} for the available contaminant fraction and for the bulk sediment. K_{OC} for the resistant fraction was found by difference. The procedure is further described as follows:

By taking the bulk sediment concentration times the fraction considered to be labile, the available contaminant concentration was obtained. The available contaminant concentration was divided by the DOC corrected pore water concentration (assuming the dissolved contaminants derived solely from the labile contaminant fraction) and the f_{oc} for the bulk sediment to obtain K_{OC} for the available contaminant fraction (Equation 8-8).

$$K_{OC,Avail} = \frac{C_{i,Sed\ Avail} \big/ C_{i,PWC}}{f_{OC}} \tag{8-8}$$

The observed K_{OC} is given by:

$$K_{OC,Obs} = \frac{K_{d,Obs}}{f_{OC}} \tag{8-9}$$

Assuming the observed K_{OC} is the proportional sum of the $K_{OC,\,Avail}$ and the $K_{OC,\,Resist}$, $K_{OC,\,Resist}$ is obtained from:

$$K_{OC,\mathrm{Re}sist} = \frac{K_{OC,Obs} - K_{OC,Avail}(1 - f_{resist})}{f_{resist}} \tag{8-10}$$

Once the desorption resistant sediment concentration ($C_{iSed,Resist}$) and the $K_{OC,\,Resist}$ are known, the desorption resistant equilibrium pore water concentration ($C_{i,PW,Resist}$) can be obtained from:

$$C_{iPW,\mathrm{Re}sist} = \frac{C_{iSed,\mathrm{Re}sist}}{K_{OC,\mathrm{Re}sist}} \tag{8-11}$$

Assuming the desorption resistant pore water concentration represents the equilibrium concentration for the soot phase, the phase specific distribution coefficient for the soot ($K_{d,Soot}$) can then be estimated, as follows:

$$K_{d,Soot} = \frac{C_{i,Soot}}{C_{i,PW\,\mathrm{Re}sist}} \tag{8-12}$$

Where $C_{i,Soot}$ is the regression coefficient (soot associated contaminant concentration) obtained from the ENTROPY regression conducted on the fractionation data (Equation 8-1). There were a few compounds for which the desorption-resistant fraction was not obtained. For these compounds, the equilibrium pore water concentration was estimated based on the mean fraction of the pore water concentration corresponding to the equilibrium pore water concentration of the desorption-resistant fraction for the other compounds.

OG and OC were assumed to be distinct but equally labile phases, in equilibrium with the pore water. The equality expressed by Equation 8-6 therefore applies, giving the following expression for OG and OC distribution coefficients:

$$K_{D_{OG}} = \frac{C_{i_{OG}}}{C_{i_{PW,Avail}}}, \quad K_{D_{OC}} = \frac{C_{i_{OC}}}{C_{i_{PW,Avail}}} \tag{8-13}$$

Where $C_{i,PW,Avail}$ is the measured pore water concentration corrected for DOC and processing losses.

Equivalence of Phase Specific Coefficients to Observed Coefficients. The weighted sum of the phase specific distribution coefficients was calculated and compared to the observed distribution coefficient as follows:

$$K_{D_{SUM}} = K_{D_{OG}} f_{OG,SED} + K_{D_{Soot}} f_{Soot,SED} + K_{D_{OC}} f_{OC,SED} \quad (8\text{-}14)$$

where

$f_{OG,SED}$, $f_{Soot,SED}$, & $f_{OC,SED}$ = the mass fraction of each phase relative to the bulk sediment mass

Two values were calculated for $K_{D,SUM:}$ one obtained by using a uniform pore water concentration for all three phases ($K_{D,SUM1}$), and one using nonuniform pore water concentrations accounting for desorption resistance and equivalence of labile phases as expressed by Equation 8-6 ($K_{D,SUM2}$). $K_{D,SUM1}$ corresponds algebraically to $K_{D,Obs}$, as illustrated in Equations 8-15 to 8-17.

$$K_{D_{SUM1}} = \frac{C_{i,OG}}{C_{i,PW}} f_{OG,SED} + \frac{C_{i,Soot}}{C_{i,PW}} f_{Soot,SED} + \frac{C_{i,OC}}{C_{i,PW}} f_{OC,SED} \quad (8\text{-}15)$$

$$K_{D_{SUM1}} = \frac{C_{i,OG}}{C_{i,PW}} \frac{M_{OG}}{M_{SED}} + \frac{C_{i,Soot}}{C_{i,PW}} \frac{M_{Soot}}{M_{SED}} + \frac{C_{i,OC}}{C_{i,PW}} \frac{M_{OC}}{M_{SED}} \quad (8\text{-}16)$$

$$K_{D_{SUM1}} = \frac{1}{C_{i,PW} M_{SED}} \left[M_{i,OG} + M_{i,Soot} + M_{i,OC} \right] = \frac{1}{C_{i,PW}} \frac{M_{i,SED}}{M_{SED}} = \frac{C_{i,SED}}{C_{i,PW}} = K_{D_{Obs}} \quad (8\text{-}17)$$

$K_{D,SUM2}$ (based on Equations 8-12 and 8-13) is not algebraically equivalent to $K_{D,Obs}$, however.

$$K_{D_{SUM2}} = \frac{C_{i,OG}}{C_{i,PW,OG}} f_{OG,SED} + \frac{C_{i,Soot}}{C_{i,PW,Soot}} f_{Soot,SED} + \frac{C_{i,OC}}{C_{i,PW,OC}} f_{OC,SED} \quad (8\text{-}18)$$

Putting in similar form to Equation 8-17, Equation 8-18 can be expressed as:

$$K_{D_{SUM2}} = \frac{1}{M_{SED}} \left(\frac{M_{i_{OG}}}{C_{i_{PW,OG}}} + \frac{M_{i_{Soot}}}{C_{i_{PW,Resistant}}} + \frac{M_{i_{OC}}}{C_{i_{PW,OC}}} \right) \quad (8\text{-}19)$$

The denominator of the soot term as defined by Equation 8-11 is very small, which must result in a larger soot coefficient than that obtained with Equation 8-17. It is evident that Equation 8-19 is not algebraically equivalent to Equation 8-17. Different values produced by the two approaches therefore reflect the different assumptions in the derivation of the values rather than a fundamental error in the predicted distributions.

The weighted sum of the phase specific coefficients divided by the mass fraction of total organic carbon yields a predicted K_{OC} value. For the uniform pore water assumption, the

predicted coefficient ($K_{OC,SUM1}$) is algebraically equivalent to the observed coefficient (Equation 8-20). For the nonuniform pore water assumption, $K_{OC,SUM\,2}$ is given in Equation 8-21.

$$K_{OC_{SUM\,1}} = K_{OC_{Obs}} = \frac{K_{D_{Obs}}}{f_{TOC}} = \frac{C_{i,OG}}{C_{i,PW}} f_{OG_{TOC}} + \frac{C_{i,Soot}}{C_{i,PW}} f_{Soot_{TOC}} + \frac{C_{i,OC}}{C_{i,PW}} f_{OC_{TOC}} \quad (8\text{-}20)$$

$$K_{OC_{SUM\,2}} = \frac{C_{i,OG}}{C_{i,PW,OG}} f_{OG_{TOC}} + \frac{C_{i,Soot}}{C_{i,PW,Soot}} f_{Soot_{TOC}} + \frac{C_{i,OC}}{C_{i,PW,OC}} f_{OC_{TOC}} \quad (8\text{-}21)$$

The coefficients $f_{OG,TOC}$, $f_{Soot,TOC}$ and $f_{OC,TOC}$ are the mass fraction of total organic carbon reflected by each of the sorptive phases (where TOC is the sum of the sorptive phases). For both forms (uniform and nonuniform pore water), the difference between K_d and K_{OC} expressions is reflected in the coefficients to the phase specific distribution coefficients. K_d coefficients reflect mass fraction of sorptive phases with respect to sediment mass, as compared to K_{OC} coefficients, which reflect mass fraction of sorptive phases with respect to TOC ($f_{OG,SED}$ as compared to $f_{OG,TOC}$ as in Equations 8-15 and 8-20).

The labile K_{OC} was compared to the phase specific coefficient for organic carbon, and for organic carbon and oil and grease combined, to evaluate the assumption that these phases contain labile contaminants. $K_{d,\,Soot}$ values were compared to the desorption-resistant distribution coefficient $K_{d,\,Resist}$. Predicted contaminant mass for each of the phases was also regressed against the desorption-resistant contaminant mass to assess possible contributions of each phase to the desorption-resistant fraction.

RESULTS

Visual Inspection of Sediments. Visual inspection of the sediments suggests phases that may be important in sorption of hydrophobic contaminants. Cinders and coal particles can be readily visualized in the coarser fraction of Calumet River (Figure 8-1). Little organic debris is present. The finer fraction appears to have a large proportion of similar hard carbon particles, and exhibits a definite luster (Figure 8-2). New Bedford contains less organic debris in the coarse fraction than New York, but more than Calumet (Figure 8-3). Some small hard carbon particles can be visualized, but are much less abundant than in Calumet. The finer fraction of New Bedford also appears to contain some hard carbon particles, but does not demonstrate the luster of Calumet (Figure 8-4). The coarse fraction of the New York sediment contains abundant organic debris, such as leaf litter and twigs (Figure 8-5). The sand is brown and gray in color, appearing to contain few or no hard carbon particles. Few hard carbon particles are apparent in the fine fraction of New York (Figure 8-6). Neither New York nor New Bedford sediments contain many large sand or small gravel particles.

FIGURE 8-1. Calumet 500 µm - 4.75 mm particles – gravel, coal, shell and cinders.

FIGURE 8-2. Calumet 250 - 500 µm particles – sand, many shiny hard carbon particles.

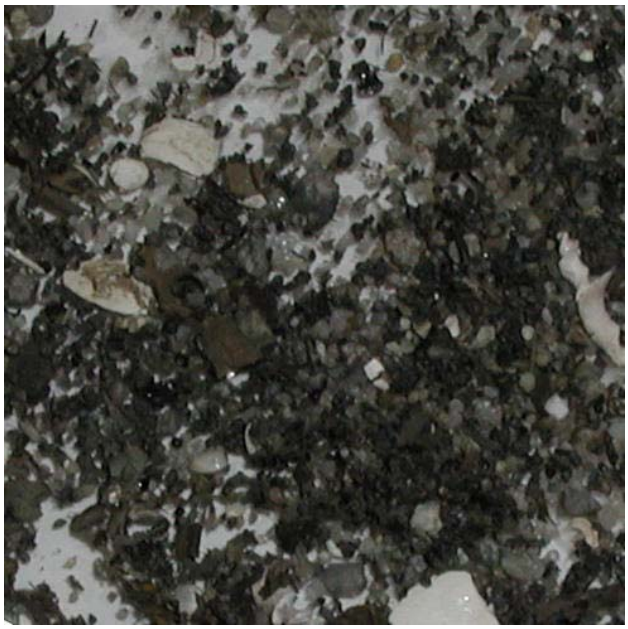

FIGURE 8-3. New Bedford 500µm - 4.75 mm particles – few small black particles, shell, minimal organic debris.

FIGURE 8-4. New Bedford 250 - 500 µm particles – sand, some shiny black particles.

FIGURE 8-5. New York 500µm - 4.75 mm particles – shell, organic debris.

FGURE 8-6. New York 250 - 500 µm particles – sand.

Pore Water Concentrations. In a number of cases, for both contaminant groups, negative pore water concentrations resulted when DOC associated contaminant mass was deducted from total contaminant mass in the pore water. This was particularly problematic when DOC adjustments were based on the theoretical K_{OC}. This suggests that the sorption to the organic carbon present in these sediments is not as high as predicted by Equations 8-2, 8-3 and 8-4. This may be due to the composition of the organic carbon. Hwang and Cutright (2004) demonstrated that DOC transport may not be significant for PAHs if the organic carbon is not aromatic in character. The OC contaminant concentration obtained from regression of the sediment data was therefore considered to be a better estimate of DOC associated contaminant levels for these sediments and was used to adjust pore water concentrations. For the selected model (Equation 8-1) this produced positive adjusted pore water concentrations for most compounds.

Observed and Predicted Coefficients. The weighted sum of phase specific distribution coefficients obtained using a uniform pore water concentration ($K_{d,\ SUM\ 1}$) corresponded well to observed coefficients for the bulk sediment ($K_{d,Obs}$). Mean difference between observed and predicted distribution coefficients for the uniform pore water concentration was 0.03 log units, with a minimum difference of 0 log units and maximum of 0.14 log units. The weighted sum of the phase specific coefficients (log $K_{d,SUM\ 2}$), calculated based on the nonuniform pore water assumption, however, exceeded observed distribution coefficients by 0.11- to 1.37-log units, with a mean difference of 0.69 log units. Because the sum of the contaminant mass predicted in the sorptive phases corresponded very well with the observed bulk sediment contaminant mass (Chapter 7), the principal difference is attributed to the pore water assumptions. The resulting expressions for $K_{D,SUM\ 2}$ and $K_{d,Obs}$ (Equations 8-19 and 8-17, respectively) are not algebraically equivalent, as previously illustrated. These results suggest that the contribution of the respective phases to the pore water concentration may be relatively complex, and differences between reported intrinsic values and environmental values may in large part be due to imbedded differences in the manner in which the coefficients are calculated. Coefficients obtained in sorption studies on single phases, for example, would correspond algebraically to coefficients calculated using a nonuniform pore water assumption, and this is reflected in the reported reference values obtained from sorption studies. All calculated coefficients are reported in Table 8-1 to illustrate the effect of specific pore water assumptions.

Correlation of the sum of the phase specific coefficients to the observed distribution coefficient ($K_{D,\ SUM1}$ vs. $K_{D,Obs}$) produced the following summary statistics: Calumet coefficient 1.04, R^2 0.997, root mean square error (RMSE) 269.58; New Bedford coefficient 1.02, R^2 0.999, RMSE 3395.9; New York coefficient 1.16, R^2 0.859, RMSE 3395.9. While RMSE is higher for New Bedford than for Calumet, observed coefficients are also an order of magnitude or more higher, thus reflecting a comparable level of error. This is not the case for New York, where the results reflect increasing divergence from the mean as the values increase. This trend was observed in regression on the sediment data to obtain the phase specific contaminant concentrations as well and reflects the characteristics of this data set rather than the influence of the pore water concentration assumption. The observed coefficients for New York are comparable to those obtained for Calumet. The RMSE resulting for New York therefore reflects roughly an order of magnitude greater error than for either of the other sediments.

TABLE 8-1. Log Octanol-Water, Theoretical, Observed and Predicted Distribution Coefficients, Equal and Nonuniform Pore Water Assumptions

Sediment	Compound	Theoretical			Observed[1]		Mean Predicted Values									
							Uniform Pore Water Assumption					Nonuniform Pore Water Assumption				
Pore Water Assumption		K_{OC}	K_{OW}	K_d	K_d	K_{OC}	K_{DOG}	K_{DSOOT}	K_{DOC}	K_{DSUM}	$K_{TOC,SUM}$	K_{DOG}	K_{DSOOT}	K_{DOC}	K_{DSUM}	$K_{TOC,SUM}$
Calumet	Acenaphthene	3.71	3.92	2.07	2.83	3.79	4.70	4.25	3.54	2.92	3.88	4.70	5.47	3.54	3.75	4.71
New York				1.91	1.8	3	4.12	3.42	2.04	1.8	3	4.12	4.76	2.04	2.67	3.86
Calumet	Acenaphthylene	3.79	4	2.15	2.83	3.79	4.67	4.24	3.55	2.91	3.87	4.67	5.46	3.55	3.74	4.70
Calumet	Anthracene	4.29	4.5	2.65	3.53	4.48	5.28	4.99	4.19	3.59	4.55	5.28	6.64	4.19	4.90	5.86
New York				2.49	3.28	4.47	5.53	4.77	3.76	3.24	4.44	5.53	6.53	3.76	4.41	5.61
Calumet	Benzo[a]anthracene	5.49	5.7	3.85	3.58	4.54	5.61	4.86	4.05	3.6	4.56	5.61	5.87	4.05	4.20	5.16
New Bedford[2]				3.81	4.44	5.46	6.58	5.76	5.20	4.51	5.54	6.58	6.92	5.20	4.74	5.77
New York				3.69	3.99	5.19	6.31	5.53	4.36	3.98	5.18	6.31	6.9	4.36	4.81	6.00
Calumet	Benzo[a]pyrene	5.83	6.04	4.19	3.42	4.38	5.34	4.85	3.76	3.43	4.39	5.34	5.9	3.76	4.19	5.15
New Bedford[2]				4.15	4.22	5.25	6.08	5.56	5.00	4.18	5.2	6.08	6.72	5.00	4.47	5.49
Calumet	Benzo[b]fluoranthene	5.99	6.2	4.35	3.59	4.55	5.56	4.88	4.11	3.6	4.56	5.56	5.97	4.11	4.28	5.24
New Bedford[2]				4.31	4.31	5.33	6.20	5.31	5.17	4.31	5.34	6.20	6.44	5.17	4.45	5.47
Calumet	Benzo[g,h,i]perylene	6.49	6.7	4.85	4.16	5.12	5.93	5.6	4.68	4.17	5.13	5.93	6.66	4.68	4.94	5.90
New Bedford[2]				4.81	5.31	6.33	7.14	6.34	6.21	5.32	6.35	7.14	7.54	6.21	5.49	6.51
Calumet	Benzo[k]fluoranthene	5.99	6.2	4.35	3.36	4.32	5.10	4.74	3.96	3.36	4.32	5.10	5.72	3.96	4.02	4.98
New Bedford[2]				4.31	3.93	4.96	5.75	4.83	4.82	3.93	4.95	5.75	5.98	4.82	4.05	5.07
Calumet	Chrysene	5.49	5.7	3.85	3.58	4.54	5.58	4.86	4.05	3.59	4.54	5.58	6.08	4.05	4.37	5.33
New Bedford[2]				3.81	4.86	5.89	6.73	5.85	5.73	4.86	5.89	6.73	7.4	5.73	5.16	6.19
New York[2]				3.69	4	5.2	6.31	5.56	4.36	3.99	5.19	6.31	7.09	4.36	4.99	6.18
Calumet	Dibenzo[a,h]anthracene	6.49	6.7	4.85	3.63	4.59	5.40	5.23	3.98	3.69	4.65	5.40	6.19	3.98	4.46	5.42
Calumet	Fluoranthene	5.01	5.22	3.37	3.51	4.47	5.48	4.77	4.12	3.54	4.5	5.48	5.99	4.12	4.29	5.25
New York				3.21	3.61	4.81	5.90	5.13	4.11	3.6	4.8	5.90	6.48	4.11	4.40	5.59
Calumet	Fluorene	3.99	4.2	2.35	3.24	4.2	5.09	4.67	3.94	3.32	4.28	5.09	5.89	3.94	4.17	5.13
Calumet	Indeno[1,2,3-c,d]pyrene	6.44	6.65	4.8	3.6	4.56	5.48	5	4.21	3.65	4.61	5.48	6.22	4.21	4.50	5.46
New Bedford[2]				4.76	3.97	5	6.11	4.79	4.64	3.99	5.02	6.11	5.94	4.64	4.09	5.11
Calumet	2-Methylnaphthalene	3.65	3.86	2.01	5.58	6.54	7.59	7.12	6.19	5.72	6.68	7.59	8.34	6.19	6.61	7.57
Calumet	Naphthalene	6.44	6.65	4.8	4.84	5.8	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)
Calumet	Phenanthrene	4.25	4.46	2.61	3.69	4.65	5.28	5.05	4.46	3.72	4.68	5.28	6.31	4.46	4.59	5.55
Calumet	Pyrene	4.89	5.1	3.25	3.59	4.55	5.55	4.72	4.25	3.6	4.56	5.55	5.95	4.25	4.27	5.23
New Bedford				3.21	5.04	6.06	6.85	5.92	5.92	5.02	6.05	6.85	7.41	5.92	5.26	6.28
New York				3.09	3.73	4.93	5.98	5.25	4.34	3.73	4.92	5.98	6.69	4.34	4.60	5.80

[1] Mean observed values. [2]Distribution coefficient calculated using estimated pore water concentration (flagged as J values)
(a) Entropy regression was not successful in producing coefficients for naphthalene

The observed TOC normalized distribution coefficients were plotted against the weighted sum of the phase specific distribution coefficients (Figures 8-7 to 8-9), also normalized to TOC. (TOC is expressed as sum of the three sorptive phases. $K_{OC, SUM\ 1}$ reflects uniform pore water assumption, $K_{OC, SUM\ 2}$, the nonuniform pore water assumption). Compounds dibenzo[a,h]anthracene and fluoranthene were excluded from the plot for New Bedford (Figure 8-8), as negative pore water concentrations were obtained for these compounds when adjusted for DOC.

Relative Magnitude of Phase Specific Coefficients. For all sediments and the uniform pore water concentration, the phase specific coefficient was larger for the OG phase than for either soot or OC in all cases, ranging from 0.17- to 1.33-log units higher than soot, with a mean of 0.65 log units. OG coefficients ranged from 0.82- to 2.08-log units greater than OC, with a mean of 1.35-log units. Similarly, the soot coefficient was larger than the OC coefficient, with two principal exceptions, having a maximum difference of 1.38-log units and a mean difference of 0.7-log units. In the New Bedford sediment, for pyrene, the soot and OC coefficients were equal, and for benzo[k]fluoranthene, the OC coefficient was only 0.01-log unit smaller than the soot coefficient.

For the nonuniform pore water assumption, the soot coefficient was generally larger than OG, with a mean difference of 0.61-log units, ranging from 1.36-log units higher to 0.17-log units lower than OG. Soot coefficients were larger than OC coefficients in all cases, ranging from 1.16-log units to 2.77-log units higher, with a mean difference of 1.96-log units.

Labile and Desorption Resistant Fraction - Coefficient Comparisons. The ratio of the available fraction distribution coefficient to the observed organic carbon normalized coefficient ($K_{OC, Avail}$ /$K_{OC, Obs}$) ranged from 0.60 to 0.96, with a mean of 0.87. These ratios are comparable to results obtained by Chai, Kochetkov and Reible (unpublished) in a similar study of three different sediments (Table 8-2).

If the assumption that the OC and OG are labile phases is correct, the ratio of the distribution coefficients for these phases should correspond to $K_{OC,Avail}$. Coefficient ratios less than one suggest that another phase may also contribute to the labile fraction. The mean ratio of the OC coefficient to the coefficient for the available fraction ($K_{d,OC}$ /$K_{OC, Avail}$, uniform pore water) was 1.07, ranging from 0.89 to 1.53. The mean ratio of the combined coefficient for organic carbon and oil and grease to available fraction ($K_{d, OCOG}$/$K_{OC, Avail}$, uniform pore water) was 1.15, ranging from 1.02 to 1.60. This suggests that the distribution of the labile phase may be more complex than assumed. Of 15 compounds for which values were available for comparison, the ratio of $K_{d,OC}$ /$K_{OC, Avail}$ was less than 1 for only five, including one for which the ratio was 0.99. For these five compounds, the ratio of the combined OG and OC coefficients to the available fraction coefficient was greater than one in all cases, although no more than 11% greater, and in two cases was within 2%. For the nonuniform pore water assumption, predicted OG and OC coefficients were unchanged.

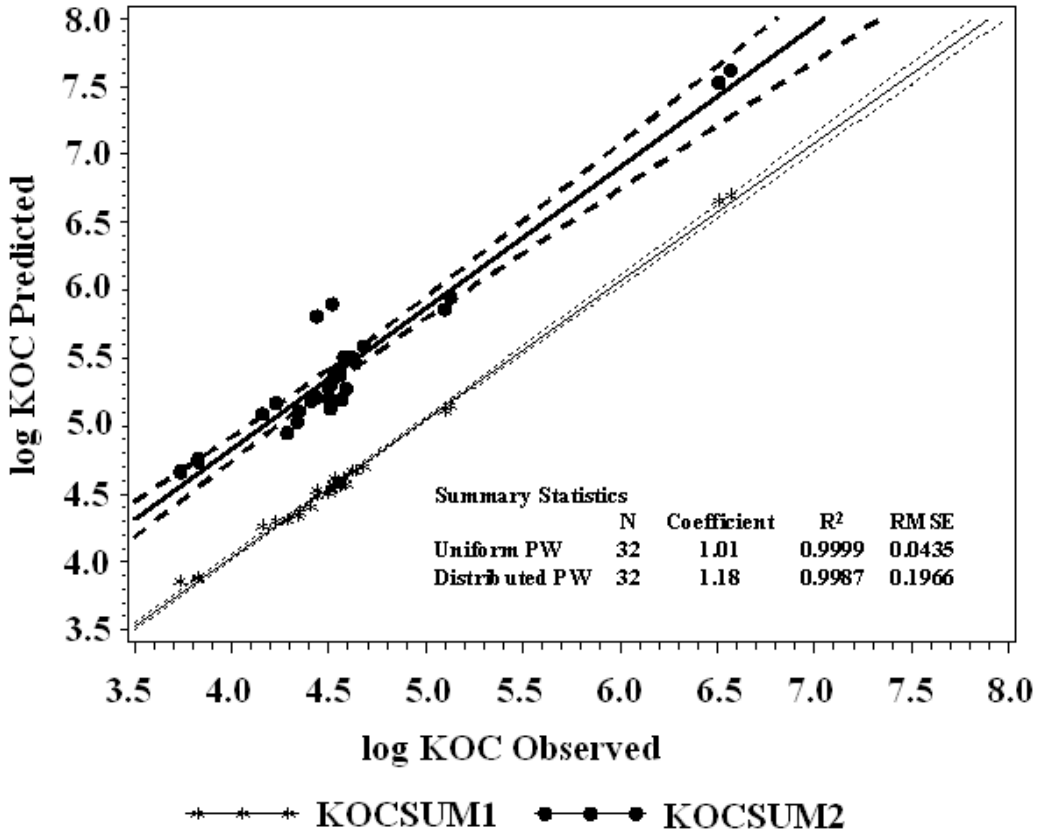

FIGURE 8-7. Calumet bulk sediment TOC normalized observed distribution coefficient vs. weighted sum of phase specific distribution coefficients (PAHs), with 95 percent confidence intervals.

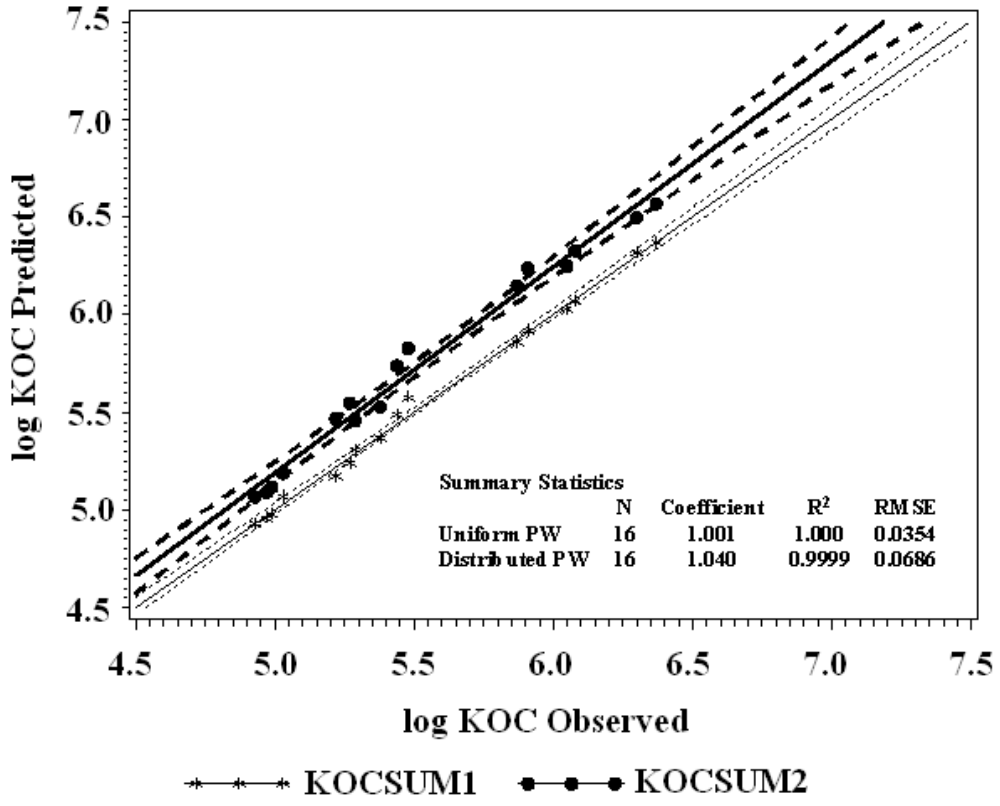

FIGURE 8-8. New Bedford bulk sediment TOC normalized observed distribution coefficient vs. weighted sum of phase specific distribution coefficients (PAHs), with 95 percent confidence intervals.

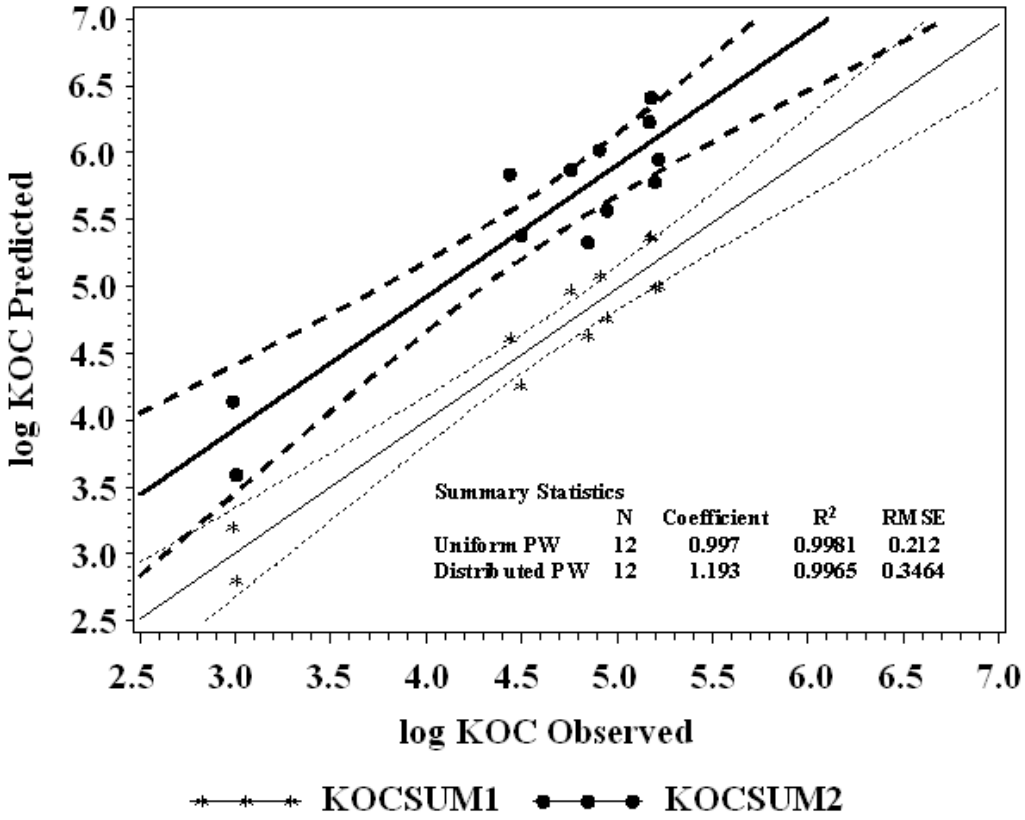

FIGURE 8-9. New York bulk sediment TOC normalized observed distribution coefficient vs. weighted sum of phase specific distribution coefficient (PAHs), with 95 percent confidence intervals.

Literature values for organic carbon normalized coefficients were also included in Table 8-2. Of particular interest are black carbon-free OC coefficients reported by Cornelissen et al. (2004b), which are considered comparable to the OC phase of the present study. Comparison of these values to the predicted $K_{d,OC}$ values reveals that they correspond within 0.06- to 0.28-log units.

The mean ratio of the predicted soot coefficient to the resistant phase coefficient was 1.03, ranging from 0.95 to 1.10 for the uniform pore water assumption. The ratio was less than 1 for only three compounds out of 15, but provides some evidence of desorption resistant fractions residing in the other sorptive phases. Cornelissen et al. (2004b) proposed a model to identify strongly sorbing non-BC OC moieties, such as the inertinite macerals, termed "opaque" OC.

Ratio of soot coefficients based on nonuniform pore water to desorption resistant coefficient ranged from 1.19 to 1.41, with a mean of 1.30, suggesting that on this basis soot could account for all of the desorption resistant contaminant fraction as well as part of the labile fraction. However, regression of desorption resistant PAH mass versus predicted PAH mass for soot shows that the contaminant mass predicted for soot is insufficient to account for the entire desorption resistant mass in these sediments, supporting a distribution over multiple phases.

Soot Coefficient Comparisons to Literature Values. Distribution coefficients obtained for soot were compared to values reported in the literature (Table 8-3). Comparative values were not found for all compounds, but predicted values appear to correspond relatively well when the grain size, carbon type, and manner in which the values were derived are taken into consideration. Predicted coefficients and representative reference values were plotted against PAH log K_{ow} values to evaluate relative trends and magnitude (Figures 8-10 to 8-12). Trendlines fitted to the reference values were uniformly positive, with the exception of the environmental values reported for Lake Ketelmeer sediments (Cornelissen et al. 2004a), which exhibited a negative slope for the two data points that were reported for anthracene and phenanthrene (log K_{ow} 3.92 and 4.46, respectively). The plot of Calumet coefficients was relatively flat overall, with a trendline slope near zero and R^2 of 0.0208. This was in part driven by the predicted coefficient for 2-methylnaphtalene, which was quite high (8.34) in view of the log K_{ow} for this compound (3.86), the lowest of the PAHs measured. The slope and R^2 value of the trendline without 2-methylnaphthalene were 0.132 and 0.143, respectively, confirming that there is not a strong relationship between log K_{ow} and K_{dSoot} for this sediment. Values did increase slightly from log K_{ow} 3.9 to 4.5, and from log K_{ow} 6.2 to 6.7 (Figure 8-10). The trendline for New Bedford coefficients displayed a negative slope (-0.528) and R^2 value of 0.194 (Figure 8-11). The plot of coefficients obtained for the New York sediment was the only one for which a trendline fitted to the data suggests a correlation to log K_{ow}, with a slope of 1.05, intercept of 1.11 and R^2 value of 0.774 (Figure 8-12). However, even for New York, the values between log K_{ow} 4.5 to 5.2 were relatively flat when considered apart from the remaining values. These trends were reflected as well for the observed coefficients for all three sediments, suggesting that sorption that occurs in the presence of multiple phases may not be governed as strongly by the hydrophobicity of the contaminant as indicated by sorption studies conducted on single sorbent phases.

Overall, observed distribution coefficients for the study sediments were lower than reference values, as were the predicted values based on the uniform pore water concentration. Predicted values based on the nonuniform pore water assumption corresponded better with the reference values, particularly for compounds with log K_{ow} less than six.

TABLE 8-2. Mean Labile and Desorption Resistant Fraction Distribution Coefficients Compared to Predicted Phase Specific Distribution Coefficients - PAHs

			Bulk Sediment log Koc			log K_{dOC}	log $K_{dOC\&OG}$	log K_{dSOOT}			
Compound	**Reference**	**Sediment**	**Theoretical**	**Mean Obs**	**Labile Fraction**	**Predicted**	**Predicted**	**Predicted[1]**		**Desorption Resistant Fraction**	**Desorption Resistant Contaminant Fraction**
Anthracene	This Study	Calumet	4.29	4.48	4.31	4.19	4.37	4.99	6.64	4.71	0.337
		New York	4.29	4.47	4.23	3.76	4.37	4.77	6.53	4.67	0.428
	Chai, Kochetkov & Reible (Unpublished)	Indiana Harbor		5.1	4.56					5.36	
		Utica Harbor		4.96	4.4					5.1	
		Rouge River		4.84	4.49					5.06	
	Karikhoff 1981	Unspecified		4.2							
Benzo[a]pyrene	This Study	Calumet	5.83	4.38	3.42	3.76	4.19	4.85	5.9	4.42	0.89
		New Bedford	5.83	5.25		5	5.19	5.56	6.72		
	Chai, Kochetkov & Reible (Unpublished)	Indiana Harbor		6.04						6.46	
		Utica Harbor		6.7	6.13					7.28	
		Rouge River		6.34	5.86					6.86	
	Reeves et al. 2004	SC1		5.34, 5.2, 5.36[a]							0.86
		SC1		5.36, 5.13, 5.05[a]							0.76
		CF1		6.12, 6.18, 6.22[a]							0.86
		CF2		5.84, 5.96, 6.56[a]							0.89
Benzo[b]fluoranthene	This Study	Calumet	5.99	4.55	3.74	4.11	4.46	4.88	5.97	4.61	0.847
		New Bedford	5.99	5.33	4.4	5.17	5.34	5.31	6.44	5.38	0.882
		New York	5.99	(a)							0.845
	Chai, Kochetkov & Reible (Unpublished)	Indiana Harbor		6.01						6.14	
		Utica Harbor		6.58	6.25						
		Rouge River		6.21	5.79					6.3	
Benzo[k]fluoranthene	This Study	Calumet	5.99	4.32	2.59	3.96	4.16	4.74	5.72	4.32	0.981
		New Bedford	5.99	4.96		4.82	4.96	4.83	5.98		
	Chai, Kochetkov & Reible (Unpublished)	Indiana Harbor		6.22						6.58	
		Utica Harbor		6.65	5.72					7.17	
		Rouge River		6.31	5.86						
Chrysene	This Study	Calumet	5.49	4.54		4.05	4.45	4.86	6.08		
		New Bedford	5.49	5.89	5.62	5.73	5.89	5.85	7.4	6.07	
		New York	5.49	5.2	4.77	4.36	5.11	5.56	7.09	5.33	
	Chai, Kochetkov & Reible (Unpublished)	Indiana Harbor		5.62						5.95	
		Utica Harbor		6.32	5.77					6.73	
		Rouge River		6.03	5.62					5.99	

(continued)

(TABLE 8-2. continued)

Compound	Reference	Sediment	Bulk Sediment log Koc			log K_{dOC}	log $K_{dOC\&OG}$	log K_{dSOOT}			Desorption Resistant Contaminant Fraction
			Theoretical	Mean Obs	Labile Fraction	Predicted	Predicted	Predicted[1]		Desorption Resistant Fraction	
Phenanthrene	This Study	Calumet	4.25	4.65	4.17	4.46	4.56	5.05	6.31	4.77	0.666
	Chai, Kochetkov & Reible (Unpublished)	Indiana Harbor		4.71	4.27					5.04	
		Utica Harbor		4.78	4.12					4.99	
		Rouge River		4.87	4.52					4.91	
	Karikhoff 1981	Unspecified		4.08							
	Cornelissen 2004b	VAR		4.6, 5.5[b]			4.8[c]				
		MEK		5.3, 5.4[b]							
		KUO		4.9, 5.3[b]			4.8[c]				
		HOY		4.3, 5.2[b]			4.5[c]				
		KET		4.8, 5.2[b]			4.84[c]				
	Reeves et al. 2004	SC1		4.74, 4.34, 4.44[a]							0.36
		SC1		4.12, 4.5, 3.94[a]							0.46
		CF1		5.26, 5.45, 5.78[a]							0.67
		CF2		5.33, 5.31, 5.47[a]							0.7
Pyrene	This Study	Calumet	4.89	4.55	4.04	4.25	4.52	4.72	5.95	4.67	0.688
		New Bedford	4.89	6.06	5.75	5.92	6.05	5.92	7.41	6.24	0.509
		New York	4.89	4.93	4.38	4.34	4.86	5.25	6.69	5.03	0.718
	Chai, Kochetkov & Reible (Unpublished)	Indiana Harbor		5.57	4.9					6.01	
		Utica Harbor		5.4	4.79					5.97	
		Rouge River		5.43	4.94					5.64	
	Karikhoff 1981	Unspecified		4.8							
	Reeves et al. 2004	SC1		4.36, 3.65, 4.23[a]							0.17
		SC1		4.41, 4.3, 4.37[a]							0.4
		CF1		5.28, 5.13, 5.2[a]							0.49
		CF2		5.34, 5.32, 5.51[a]							0.73

[1] First value equals uniform pore water assumption; second value equals nonuniform pore water assumption.

[a] First value log Koc 5mM CaCl2 extractant; second value log KOC PO4 buffer extractant; third value log KOC TCLP extractant.

[b] First value log K_{TOC} at 1 mg/l; second value log K_{TOC} at 1 ng/l.

[c] BC free log KOC.

TABLE 8-3. Mean Predicted K_dSoot and Published Distribution Coefficients for Environmental Materials and Standard Reference Materials - PAHs

Reference	Sediment	Compound																													
		Acenapthene		Acenaphthylene		Anthracene		Benzo[a]anthracene		Benzo[a]pyrene		Benzo[b]fluoranthene		Benzo[g,h,i]perylene		Benzo[k]fluoranthene		Chrysene		Dibenzo[a,h]anthracene		Fluoranthene		Fluorene		Indeno[1,2,3]pyrene		2Methylnaphthalene		Phenanthrene		Pyrene	
This Study	Calumet[a]	4.25	5.47	4.24	5.46	4.99	6.64	4.86	5.87	4.85	5.90	4.88	5.97	5.60	6.66	4.74	5.72	4.86	6.08	5.23	6.19	4.77	5.99	4.67	5.89	5.00	6.22	7.12	8.34	5.05	6.31	4.72	5.95
	New Bedford[a]							5.76	6.92	5.56	6.72	5.31	6.44	6.34	7.54	4.83	5.98	5.85	7.40							4.79	5.94					5.92	7.41
	NewYork[a]	3.42	4.76			4.77	6.53	5.53	6.90									5.56	7.09			5.13	6.48									5.25	6.69
Jonker & Koelmans 2002	Traffic soot[b]					6.27	6.94	7.44	8.26		8.87		8.54	8.06	8.89	7.82	8.66		8.18			6.39	6.96							5.93	6.24		6.79
	Oil soot[b]					5.26	5.58	6.75	7.40		8.17		8.09	7.84	8.31	7.36	8.27		7.22			5.73	6.17							5.00	5.27		5.95
	Wood soot[b]					5.12	5.68	6.07	7.08		7.89		7.65	6.71	8.18	6.44	7.67		7.00			5.33	6.12							4.91	5.31		6.09
	Coal soot[b]					4.44	5.74	5.59	6.61		7.41		7.02	6.75	7.64	6.17	7.11		6.51			4.87	5.73							4.34	5.54		5.71
	Coal[b]					6.63	6.10	7.25	7.95		8.41		8.34	7.49	8.22	7.43	8.11		8.53			6.35	6.72							6.25	6.57		6.95
	Charcoal[b]					7.61	7.10	8.36	7.54		9.07		7.87	8.43	8.21	8.44	8.07		7.20			7.82	6.34							7.45	6.19		6.40
	Fly ash[b]					5.08		6.27						6.83		6.64						5.47								4.75			
	Activated carbon[b]					8.96		9.61						9.48		9.72						9.06								8.76			
	Graphite[b]					6.54		8.65						9.13		9.16						7.40								6.16			
	Diesel soot[b]					5.72	6.28	7.56	7.80		8.53	na	8.52	8.51	8.28	8.18	8.34		7.59			6.30	6.49							5.41	5.68		6.35
Gustafsson & Gschwend 1997	Thermodynamic Model[c]	5.80				6.7		7.8		8.4								8.2		9.3		6.9		6.2						5.8		7	
vanNoort 2003	Thermodynamic Model[d]					5.67		7.23		7.38		7.1		7.9		7.33		6.88				6.44		5.35						5.60		6.4[i]	6.47[i]
	Diesel soot																							5.34						5.68		6.55	
	Exhaust pipe soot					7.05		8.37		8.98		8.65		9		8.77		8.29				7.07										6.90	
Cornelissen et al. 2004a	Lake Ketelmeer[e]					6.24																								5.62			
	Lake Ketelmeer[e]					5.3																								4.7			
Cornelissen et al. 2004b	VAR[f]																													3.5	6.3		
	KUO[f]																													3.5	6.3		
	HOY[f]																													4	6.8		
	KET[f]																													3.2	6		
Bucheli & Gustafsson 2000	Diesel soot[g]																							5.40						5.82		6.59	
	Diesel soot[h]																							4.63						6.62		7.03	
Walters & Luthy 1984	Activated carbon[j]	7.22		6.72		6.79		7.31										8.13						7.78						7.11		7.48	

[a] First value uniform pore water concentration assumption; second value nonuniform pore water assumption. [b] First value added deuterated compound; second value native compound, on <50μm prepared sorbents (pulverized charcoal and graphite, all materials except diesel soot washed with Nanopure water containing 0.01 M CaCl2, centrifuged, decanted, dried at 80 deg C). [c] Calculated on the basis of SSABC=58m^2/g. [d] $K_{F,BC}$ Intrinsic value (combusted to remove naturally occurring organic material).

[e] $K_{F,BC}$ Environmental value (in presence of naturally occurring organic material) extrapolated from $K_{F,TOC}$ isotherms and $K_{F,BC}$ intrinsic isotherms. [f] First value log K_{BC}^{env} at 1 mg/l; second value log K_{BC}^{env} at 1 ng/l. [g] Batch study.

[h] Column study. [i] First value, model estimate for exhaust pipe soot; second value model estimate for NIST diesel soot. [j] Calculated from Henry's law constants given in mg/g.

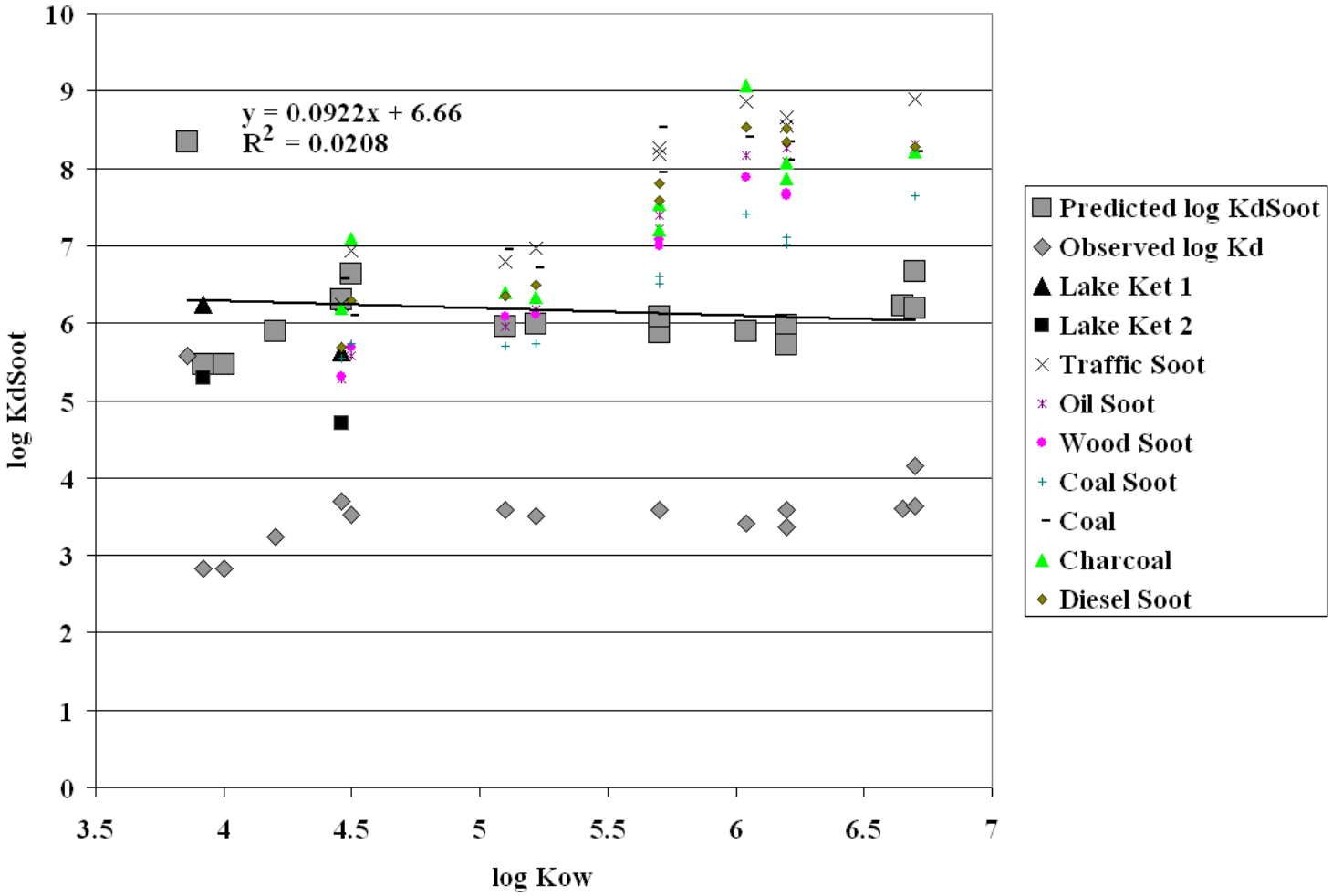

FIGURE 8-10. Calumet predicted log K_{dSoot} and available reference values versus PAH log K_{ow}.

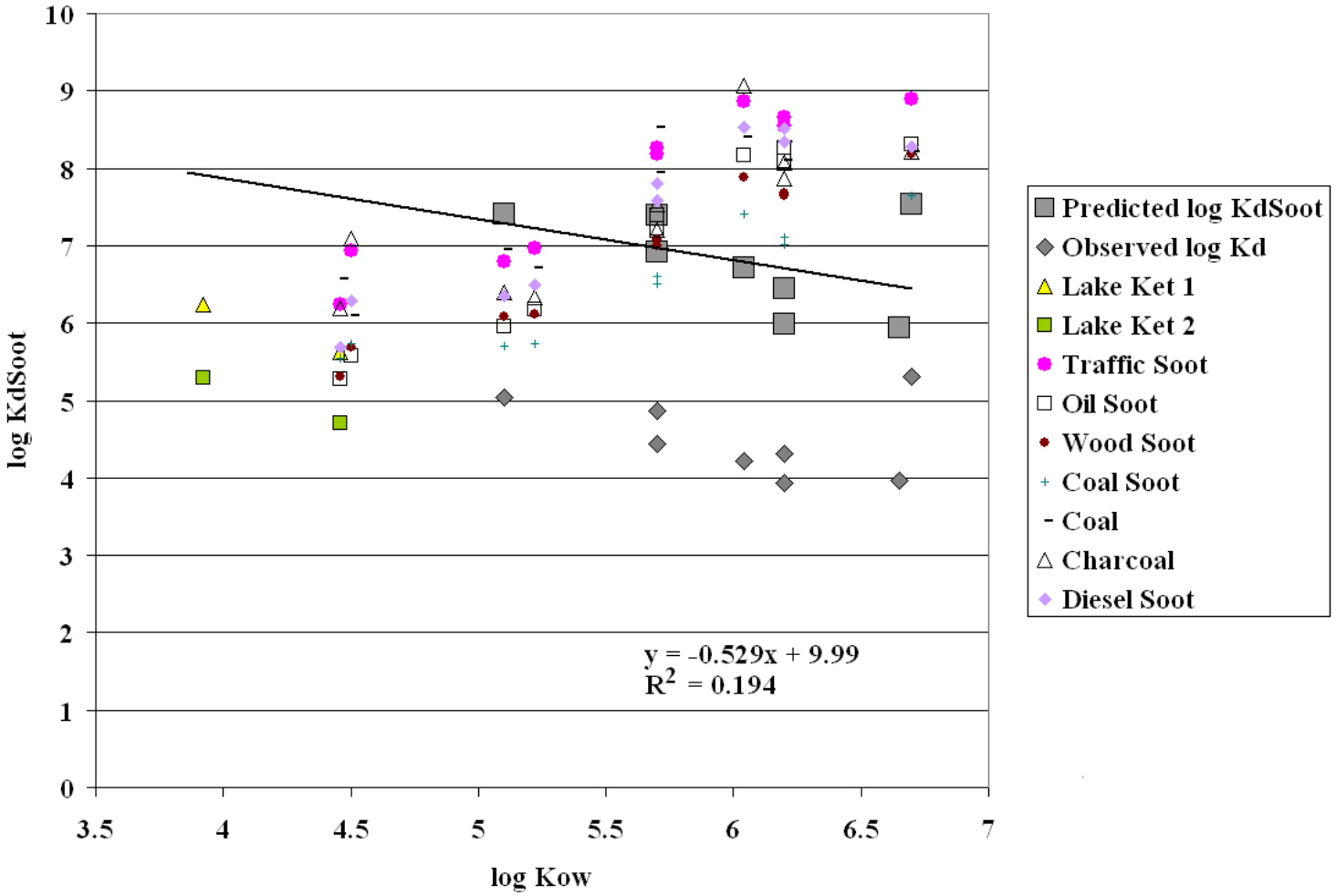

FIGURE 8-11. New Bedford predicted log K_{dSoot} and available reference values vs. PAH log K_{ow}.

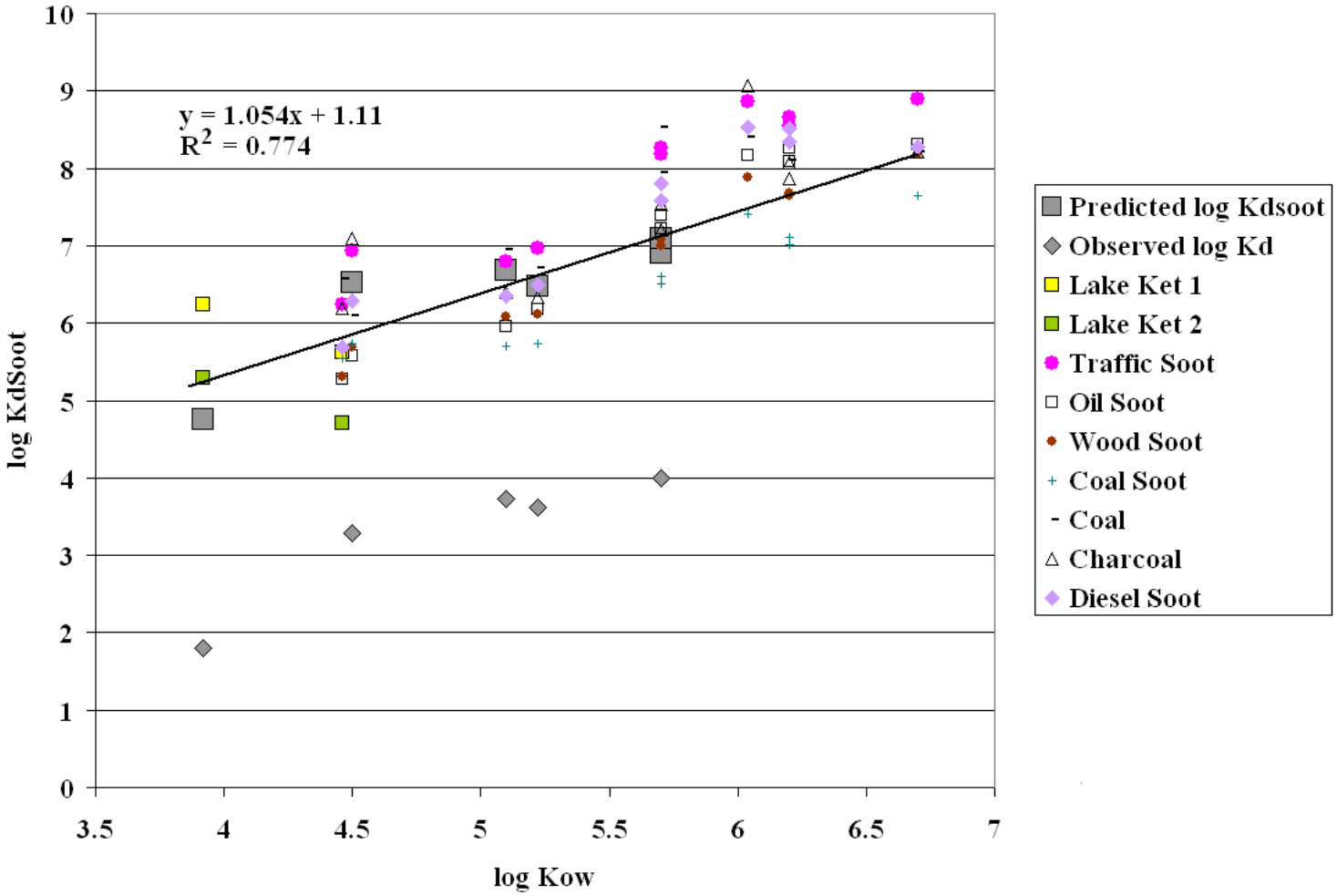

FIGURE 8-12. New York predicted log K_{dSoot} and available reference values vs. PAH log K_{ow}.

OG Coefficient Comparisons to Literature Values. Distribution of hydrophobic organic contaminants to the oil and grease phase has not been widely studied. Jonker et al. (2003) conducted a study in which natural sediments were spiked with oil and six PAHs. Half of the samples were artificially weathered, and then extracted using solid phase extraction, and oil and grease distribution coefficients calculated. The remaining samples were extracted without weathering. Coefficients reported in that paper were compared to the distribution coefficients obtained for the oil and grease fraction in this study (Table 8-4). The values obtained for the study sediments using the regression method compare favorably to those reported in Jonker et al. (2003) for unweathered samples, but were an order of magnitude or more lower than the values reported for weathered samples. The relative magnitude of the oil and grease coefficient (K_{dOG}) to the observed organic carbon normalized coefficient (K_{OC}) for the study sediments was very similar to the relative values for the weathered samples from Jonker et al. (2003) study, however. Taking into account the inherent difference in the study sediments and the sediments used by Jonker et al (2003), as reflected by the K_{OC} values, the coefficients obtained for the study sediments appear to be reasonable.

A more recent study (McNamara et al. 2005) examined the respective partitioning of PCBs to oil in the presence of natural organic matter. Distribution coefficients for partitioning to the oil phase were not given, but the authors concluded that partitioning of the PCBs to the oil exceeded partitioning to the OC by an order of magnitude. This is consistent with the relative magnitude of the OG and OC distribution coefficients obtained in the present study for PAHs and PCBs (Chapter 9).

DISCUSSION

Soot partition coefficients reported by Jonker and Koelmans (2002) for both PAHs and PCBs were for materials that had been thoroughly washed to remove floating and easily soluble fractions, then dried, ground and passed through a 50 μm sieve to produce a small particle fraction representative of that subject to atmospheric transport. Because black carbon sorption is thought to be a surface area dependent phenomenon (Cornelissen et al. 2004a), large differences in surface area between the black carbon in the study sediments and other sediments or reference values could account for some disparity in coefficient values. In all three study sediments, the highest soot concentrations were found in the sand fraction (>75 μm particles), with the next highest concentrations in the silt fraction (5 -75 μm). Because these materials are predominantly coarser than those utilized in Jonker and Koelmans (2002), they would be expected to have much lower surface area and correspondingly lower distribution coefficients. PAH coefficients obtained for the study sediments were on average 0.1 log units (New Bedford and New York) to 0.2 log units (Calumet) lower than those reported by Jonker and Koelmans (2002).

Effects of competition from naturally occurring organic materials must also be considered in comparing the reported literature values to the results obtained for the study sediments. Cornelissen et al. (2004a) reported two Freundlich coefficient values obtained from isotherm studies on natural sediments: an intrinsic and an environmental value. The intrinsic value was obtained from sediment combusted to remove natural organic material. The environmental value was derived from isotherms for the un-combusted sediment (giving $K_{F,TOC}$) and from the intrinisic coefficient ($K_{BC,int}$). Two PAHs were studied (phenanthrene and anthracene). The environmental black carbon coefficient ($K_{BC,env}$) was estimated to be a factor of 8 smaller than the intrinsic value for anthracene and a factor of 9 for phenanthrene. This

TABLE 8-4. Mean Predicted log K_{dOG} and Published Distribution Coefficients for Oil Contaminated Sediments

		Compound											
		Anthracene		Benzo[a]anthracene		Benzo[g,h,i]perylene		Benzo[k]fluoranthene		Fluoranthene		Phenanthrene	
Reference	**Sediment**	**log K_{OC}**	**K_{dOG}**	**log K_{OC}**	**K_{dOG}**	**log K_{OC}**	**K_{dOG}**	**log K_{OC}**	**K_{dOG}**	**log K_{OC}**	**K_{dOG}**	**log K_{OC}**	**K_{dOG}**
This Study	Calumet[a]	4.48	5.28	4.54	5.61	5.12	5.93	4.32	5.1	4.47	5.48	4.65	5.28
	New Bedford[a]			5.46	6.58	6.33	7.14	4.96	5.75				
	NewYork[a]	4.47	5.53	5.19	6.31					4.81	5.9		
Jonker et al. 2003	Unweathered/DMA[b]	5.71	5.15	6.28	6.39	7.23	7.01	6.84	6.97	5.34	5.11	4.68	
	Unweathered/ACL[b]		5.28		6.37		7.16		7.01		5.43		
	Unweathered/BIL[b]		5.11		6.29		6.98		6.81		5.42		
	Weathered/DMA[b]	5.49	6.92	6.55	7.24	7.4	7.1	7.09	6.96	5.63	6.51	5.19	6.86
	Weathered/ACL[b]		6.96		7.41		7.38		7.36		7.07		6.9
	Weathered/BIL[b]		6.94		7.22		6.86		6.89		6.74		6.87

[a] Uniform and nonuniform pore water assumption.

[b] DMA-distillate marine grade A gasoil; ACL-Arabian crude light crude oil; BIL-waste lubricating oil collected by skimming bilge water.

Note: Weathered indicates artificially weathered for 2 years after adding oil and prior to spiking with PAHs. Unweathered indicates spiked immediately after addition of oil. K_{doil} obtained by deducting intrinisic KOC prior to oil addition.

suggests that, generally, distribution coefficients obtained on natural sediments may reasonably be expected to be roughly an order of magnitude lower than values obtained for the pure or concentrated reference materials used in a large proportion of sorption studies, simply due to competition from natural organic materials.

The environmental BC coefficients reported by Cornelissen et al. (2004a) are considered to be most comparable to the study sediments, of those reported in Table 8-3, and are in generally good agreement with the soot coefficients reported here.

SUMMARY AND CONCLUSIONS

Good correspondence was obtained between observed K_d and the weighted sum of the predicted phase specific coefficients, using a uniform pore water concentration for calculation of each coefficient. Values calculated using a nonuniform pore water concentration based on available and desorption resistant fractions were approximately an order of magnitude higher for soot phases. Coefficients for OG and OC were unaltered by the pore water assumptions because both were assumed to be labile phases in equilibrium with the pore water. The premise that the measured pore water concentration represents the equilibrium concentration for the labile fractions is reasonable, but the distribution of labile and desorption resistant fractions among the sorptive phases does not appear to be entirely straightforward. Coefficients obtained for OC and OG, initially assumed to comprise entirely labile phases, were greater than coefficients for the available fraction either individually or in combination for a number of PAHs. Conversely, coefficients obtained for soot underpredicted the desorption resistant fraction for some compounds. A six compartment model, representing available and desorption resistant fractions in oil and grease, soot and organic carbon may better represent the physical system.

A wide range of distribution coefficients is reported in the literature for different black carbon materials. Soot distribution coefficients obtained for the study sediments based on the uniform pore water concentration were in many cases lower than published distribution coefficients for standard reference materials, although largely within the order of magnitude difference observed by other researchers for intrinisic versus environmental sorption. Differences between predicted and reported black carbon coefficients may be attributable to the effects of competition for sorption sites on the black carbon in natural sediments and to differences in type and size of black carbon in the study sediments relative to materials used in reported studies. Relatively good correspondence to reported values for environmental black carbon sorption in natural sediments was observed. Coefficients obtained using phase specific pore water concentrations were comparable to the intrinsic values reported for carbon phases representative of those expected in natural urban sediments. This is also consistent with the assertion that intrinsic and environmental coefficients are algebraically different, and that this may account for a large part of the observed differences between them.

The phase specific distribution coefficients obtained by regression of fractionation data appear to reasonably reflect contaminant distribution between the sorptive phases. Knowledge of sorptive phase partitioning is expected to be especially useful in contaminant pathway analysis as applied to materials that have been separated for the purpose of contaminant reduction. The potential mobility of the contaminants remaining in the fractions may be assessed based on the mass of sorptive phases reporting with each fraction, using the phase specific distribution coefficients.

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CHAPTER 9

PHASE SPECIFIC DISTRIBUTION COEFFICIENTS – PART 2: PCBS

INTRODUCTION

Conventional methods of deriving distribution coefficients, whether theoretical or site-specific, provide little information regarding the relative contaminant loading of each of the sorptive phases (Hansen et al. 1999; EPA 1999; Girvin and Scott 1997). Distribution coefficients may be normalized to organic carbon, but organic carbon itself may be composed of several different phases, each with different properties (Cornelissen et al. 2004a and b; Hwang and Cutright 2004). Oil and grease, soot and organic carbon all comprise a portion of the total organic carbon (TOC) measurement, yet partitioning to these phases and bioavailability may be vastly different (Jonker et al. 2003). The ultimate disposition of each of these phases as a consequence of treatment may also be different and may determine the effectiveness of treatment (Olin-Estes et al. 2002). Direct measurement of phase specific contaminant concentrations, however, is not practical due to the difficulty of separating the sorptive phases in quantities sufficient for analysis and without destroying the compounds of interest.

Fractionation studies were conducted on three natural sediments in order to obtain differential measurements of PAHs, PCBs, and sorptive phases. Data obtained from these studies was used to establish correlations between contaminant mass and mass of the sorptive phases (Chapter 7). The resulting model was used to develop phase specific distribution coefficients. Results obtained were compared to the observed distribution coefficients for these sediments, as well as theoretical and organic carbon normalized values, and values reported in the literature for partitioning to oil and grease, soot and TOC. Results obtained for PCBs are reported in this chapter. Results obtained for PAHs were reported in Chapter 8.

METHODS

Fractionation Studies and Correlations. Fractionation studies were conducted on three natural sediments, obtained from Calumet River, New York Harbor and New Bedford Harbor. The sediments were homogenized and then separated into three operationally defined size fractions and two density fractions (Chapters 5 and 6). Contaminant concentrations and concentration of sorptive phases were measured in each fraction and in the bulk sediment. The data was then analyzed to assess statistical correlations between contaminant distribution and the sorptive phases (Chapter 7). A linear model was obtained expressing the distribution of the contaminant mass with respect to the sorptive phases:

$$M_i = C_{i_{OG}} * M_{OG} + C_{i_{Soot}} * M_{Soot} + C_{i_{OC}} * M_{OC} \qquad (9\text{-}1)$$

where

M_i = mass of contaminant i in the bulk sediment or operationally defined fraction (μg/kg)

C_{iOG}, C_{iSoot} and C_{iOC} = concentration of contaminant i in the oil and grease (OG), soot and organic carbon (OC) phases (μg/kg)

M_{OG}, M_{Soot} and M_{OC} = mass of the sorptive phases in the bulk sediment and operationally defined size and density fractions (kg)

Visual Phase Identification. Small samples of each sediment were washed through sieves to separate the 250 - 500 μm particles and the 500 μm - 4.75 mm particles. These fractions were then dried and placed in pietre dishes for examination.

Corrections to Pore Water Concentrations. Raw data obtained from analyses of sediment and pore water in the fractionation studies were reported in Chapters 5 and 6. Pore water concentrations were adjusted for losses occurring during processing and for DOC associated contaminants. The adjusted values were used for calculation of distribution coefficients. The magnitude of sorption losses to Nalgene centrifuge containers was determined in a separate study using PCB solutions made up from standards at concentrations comparable to the pore water. These solutions were processed in a manner similar to the pore water and losses to the containers calculated as a percentage of the contaminant mass. The sorption study and procedures used to calculate adjustments for DOC associated contaminants were more fully desribed in Chapter 8.

Observed Distribution Coefficient. The observed distribution coefficient is given as:

$$K_{D_{OBS}} = C_{i_{Bulk}} / C_{i_{PWC}} \tag{9-2}$$

where

C_{iBulk} = concentration of contaminant i in the bulk sediment (μg/kg)
C_{iPWC} = concentration of contaminant i in the pore water, corrected for sorption losses and DOC (using the model specific organic carbon concentration) (μg/L)

Phase Specific Distribution Coefficients. Distribution coefficients were obtained for oil and grease, soot and organic carbon using the phase specific contaminant concentrations determined previously by regression of the fractionation data (Chapter 7) and the DOC adjusted pore water concentration. Two cases were used in calculating the phase specific distribution coefficients: 1) each phase was assumed to be in equilibrium with the pore water at the measured concentration (uniform pore water assumption), and 2) the dissolved concentration was assumed to be largely attributable to the labile phases (nonuniform pore water assumption). Case 2 implies that the labile phases are in equilibrium with the pore water while the non-labile phase is not (slow sorption to this phase is occuring).

The algebraic equivalence of the observed distribution coefficient and coefficients derived using the uniform pore water assumption was demonstrated in Chapter 8. Coefficients derived using the nonuniform pore water assumption are not algebraically equivalent to the observed coefficients, and this was also more fully explained in Chapter 8. The point is important to recognize in interpretation of the results, not only of this study, but in comparing reported coefficients obtained from natural sediments (environmental coefficients) to those

obtained from sorption studies on single sorbents (intrinsic coefficients). Phase specific coefficients obtained using the nonuniform pore water assumption are essentially equivalent to intrinsic coefficients, as they utilize equilibrium pore water concentrations for that phase, rather than for the sediment as a whole, in calculating the coefficient. For example, if each phase is assumed to be in equilibrium with the pore water, the following equality must be satisfied:

$$\frac{C_{i_{OG}}}{K_{D_{OG}}} = \frac{C_{i_{Soot}}}{K_{D_{Soot}}} = \frac{C_{i_{OC}}}{K_{D_{OC}}} \tag{9-3}$$

Equation 9-3 derives from:

$$K_{D_{OG}} = \frac{C_{i_{OG}}}{C_{i_{PW}}}, \quad K_{D_{Soot}} = \frac{C_{i_{Soot}}}{C_{i_{PW}}}, \quad and\ K_{D_{OC}} = \frac{C_{i_{OC}}}{C_{i_{PW}}} \tag{9-4}$$

Where $C_{i,PW}$ is the same value (uniform) for each equality.

If any phase is not in equilibrium with the pore water, such as a desorption resistant phase, then the equality in Equation 9-3 no longer holds. The denominator utilized in calculating a coefficient for the desorption resistant phase must be the pore water concentration at which that phase would establish equilibrium if isolated from the other, more labile phases. This is equivalent to sorption studies conducted on single sorbents, in which the system is allowed to equilibrate to that sorbent alone.

The desorption resistant fraction was estimated based on infinite sink testing similar to that described in Pignatello (1990). That procedure and the calculations used to estimate the equilibrium pore water concentration for the desorption resistant phase are more fully described in Chapter 8. Based on observations by other researchers, the soot phase was assumed to be the desorption resistant phase, while the oil and grease (OG) and non-black carbon organic carbon (OC) were assumed to be distinct and equally labile phases. The equality expressed by Equation 9-3 therefore applies to OG and OC. The measured pore water concentration adjusted for DOC associated contaminants and for processing losses was used in calculating coefficients for both OG and OC for the nonuniform pore water assumption. The equilibrium pore water concentration for the soot phase was assumed to be equivalent to the equilibrium concentration for the desorption resistant phase.

With the nonuniform pore water assumption, the resulting denominator for the soot coefficient is very small, yielding a larger distribution coefficient than that obtained for the uniform pore water assumption.. The OC and OG coefficients are not altered by the different pore water assumptions. The effect of the pore water assumptions is important, however, when considering the composite coefficient calculated from the sorptive phases which differs considerably for the different pore water assumptions. The weighted sum of the phase specific distribution coefficients (the composite coefficient) was calculated as follows, and compared to the observed distribution coefficient:

$$K_{D_{SUM}} = K_{D_{OG}} f_{OG,SED} + K_{D_{Soot}} f_{Soot,SED} + K_{D_{OC}} f_{OC,SED} \tag{9-5}$$

where

$f_{OG,SED}$, $f_{Soot,SED}$, & $f_{OC,SED}$ = the mass fraction of each phase relative to the bulk sediment mass

For the uniform pore water assumption, Equation 9-5 and Equation 9-2 are algebraically equivalent, as previously stated, and as illustrated in Chapter 8. Good correspondence between the observed coefficient and the composite coefficient would be expected for the uniform pore water assumption if the proposed model is valid. A composite K_{OC} value (organic carbon normalized distribution coefficient) was also calculated as follows, and is equivalent to the observed organic carbon normalized coefficient:

$$K_{OC_{SUM\,1}} = K_{OC_{Obs}} = \frac{K_{D_{Obs}}}{f_{TOC}} = \frac{C_{i,OG}}{C_{i,PW}} f_{OG_{TOC}} + \frac{C_{i,Soot}}{C_{i,PW}} f_{Soot_{TOC}} + \frac{C_{i,OC}}{C_{i,PW}} f_{OC_{TOC}} \quad (9\text{-}6)$$

For the nonuniform pore water assumption, the denominators differ and the expression looks like this:

$$K_{OC_{SUM\,2}} = \frac{C_{i,OG}}{C_{i,PW,OG}} f_{OG_{TOC}} + \frac{C_{i,Soot}}{C_{i,PW,Soot}} f_{Soot_{TOC}} + \frac{C_{i,OC}}{C_{i,PW,OC}} f_{OC_{TOC}} \quad (9\text{-}7)$$

The coefficients $f_{OG,TOC}$, $f_{Soot,TOC}$ and $f_{OC,TOC}$ are the mass fraction of total organic carbon reflected by each of the sorptive phases (where TOC is the sum of the sorptive phases).

RESULTS

Visual Inspection of Sediments. Visual inspection of the sediments revealed substantial differences between the sediments and the character of the sorptive phases present. Photographs of the sediments can be found in Chapter 8 (Figures 8-1 to 8-6). On the basis of visual inspection, hard carbon sorption would be expected to be most important to Calumet, and to some extent to New Bedford. Cinders and coal particles can be readily visualized in the coarser fraction of Calumet River (Figure 8-1). Little organic debris is present. The finer fraction appears to have a large proportion of similar hard carbon particles, and exhibits a definite luster (Figure 8-2). The finer fraction of New Bedford also appears to contain some hard carbon particles, but does not demonstrate the luster of Calumet (Figure 8-4). New Bedford contains less organic debris in the coarse fraction than New York, but more than Calumet (Figure 8-3). Some small hard carbon particles can be visualized, but are much less abundant than in Calumet. Little hard carbon was visualized in New York, but abundant leaf litter and other natural organic matter was present (Figure 8-5 and 8-6). OC may therefore govern sorption behavior in the New York sediment. Calumet is the coarsest sediment of the three, with a significant sand fraction and some fine gravel present. Neither New York nor New Bedford sediments contain many large sand or small gravel particles.

Pore Water Concentrations. In a number of cases, negative pore water concentrations resulted when DOC associated contaminant mass was calculated based on the theoretical K_{OC}. This suggests that the sorption to the organic carbon present in these sediments is not as high as

predicted by Equations 8-2, 8-3 and 8-4 (Chapter 8). This may be due to the composition of the organic carbon. Hwang and Cutright (2004) demonstrated that DOC transport may not be significant for PAHs if the organic carbon is not aromatic in character. The OC contaminant concentration obtained from regression of the sediment data was used to estimate DOC associated contaminant levels and to adjust pore water concentrations.

Observed and Predicted Coefficients. The TOC normalized composite coefficient (weighted sum of the phase specific coefficients normalized to TOC) was plotted against the normalized observed distribution coefficient (Figures 9-1 to 9-3). PCBs 70 and 18 were excluded from the Calumet plot (Figure 9-1) as negative pore water concentrations were obtained for these compounds. There were no compounds for which negative pore water concentrations were obtained for New Bedford or New York. PCB 7 plotted as a true outlier for New Bedford and was eliminated from the plot, however. For the uniform pore water concentration, mean difference between $K_{d, SUM1}$ and $K_{d, Obs}$ was 0.07 log units, ranging from 0.003 to 1.32 log units (Table 9-1). As for PAHs, the composite coefficients exceeded observed distribution coefficients for the nonuniform pore water assumption (Table 9-1). Mean difference between $K_{d,SUM\,2}$ (obtained using a nonuniform pore water concentration) and $K_{d,Obs}$ was 0.41 log units, ranging from 0.07- to 1.74-log units.

Correlation of the composite coefficients to the observed distribution coefficient ($K_{D, SUM1}$ vs. $K_{D,Obs}$) produced the following summary statistics: Calumet coefficient 1.03, R^2 0.991, RMSE 199.3; New Bedford coefficient 1.06, R^2 0.994, RMSE 527.7; New York coefficient 1.12, R^2 0.787, RMSE 2408.7. RMSE was higher for New Bedford than for Calumet, but of a similar magnitude. However, New Bedford observed coefficients were also approximately an order of magnitude or more higher than Calumet. Thus, the RMSE value for New Bedford reflects a lower magnitude of error in the New Bedford coefficients. New York displayed the highest error, with increasing divergence from the mean as the values increased, similar to the results obtained for PAHs (Chapter 8).

Relative Magnitude of Phase Specific Coefficients. For the uniform pore water assumption, the phase specific coefficient was larger for the OG phase than for either soot or OC in all cases, ranging from 0.09- to 1.82-log units higher than soot, with a mean of 1.26-log units. OG coefficients ranged from 0.32- to 1.78-log units greater than OC, with a mean of 1.20-log units. The soot and OC coefficients were more comparable for PCBs than for PAHs (Chapter 8), possibly reflecting the effect of steric hindrances for non-planar PCBs in sorption to soot. The soot coefficient ranged from 0.65-log units less than the OC coefficient to 1.15-log units greater, with a mean difference of -0.06-log units.

For the nonuniform pore water assumption, the OG coefficient was smaller than the soot coefficient with the exception of seven compounds, all in the New Bedford sediment. Mean difference between OG and soot coefficients was –0.41-log units, ranging from –1.59-log units to 0.13 log units. OG coefficients were greater than OC coefficients in all cases, with a mean difference of 1.21-log units, ranging from 0.32- to 1.78-log units. Soot coefficients were also greater than OC coefficients in all cases, with a mean difference of 1.63-log units, ranging from 1.04- to 2.95-log units.

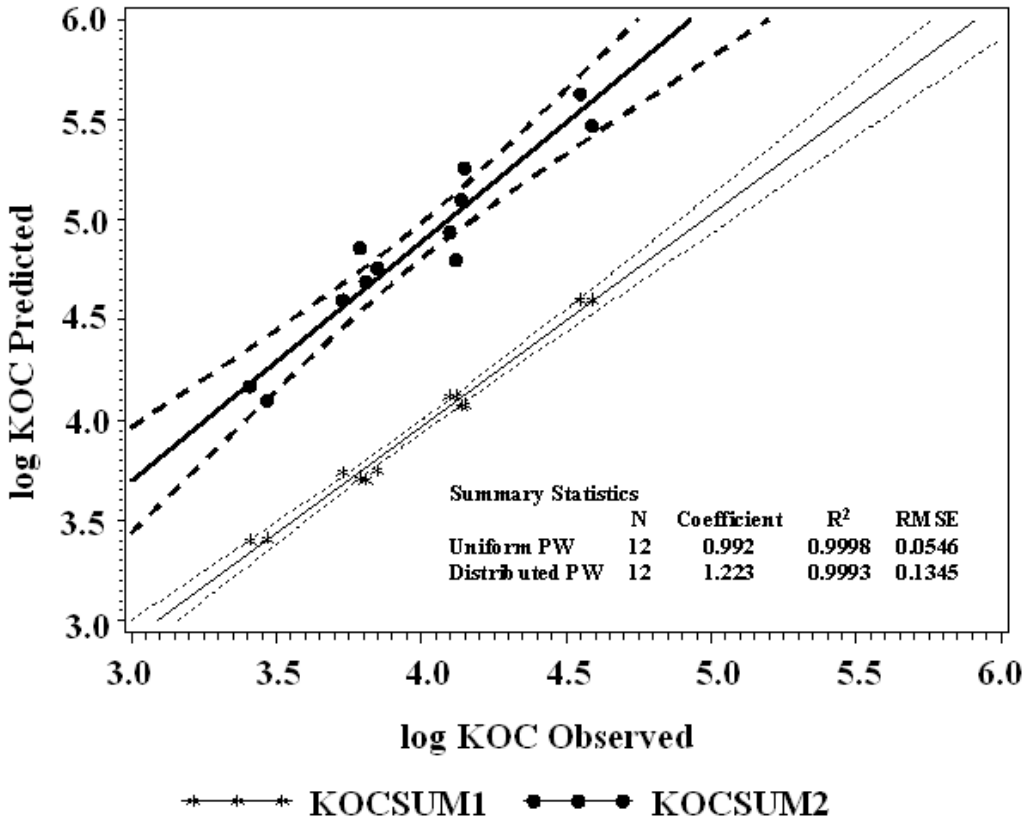

FIGURE 9-1. Calumet bulk sediment TOC normalized observed distribution coefficient vs. weighted sum of phase specific distribution coefficients (PCBs), with 95 percent confidence intervals.

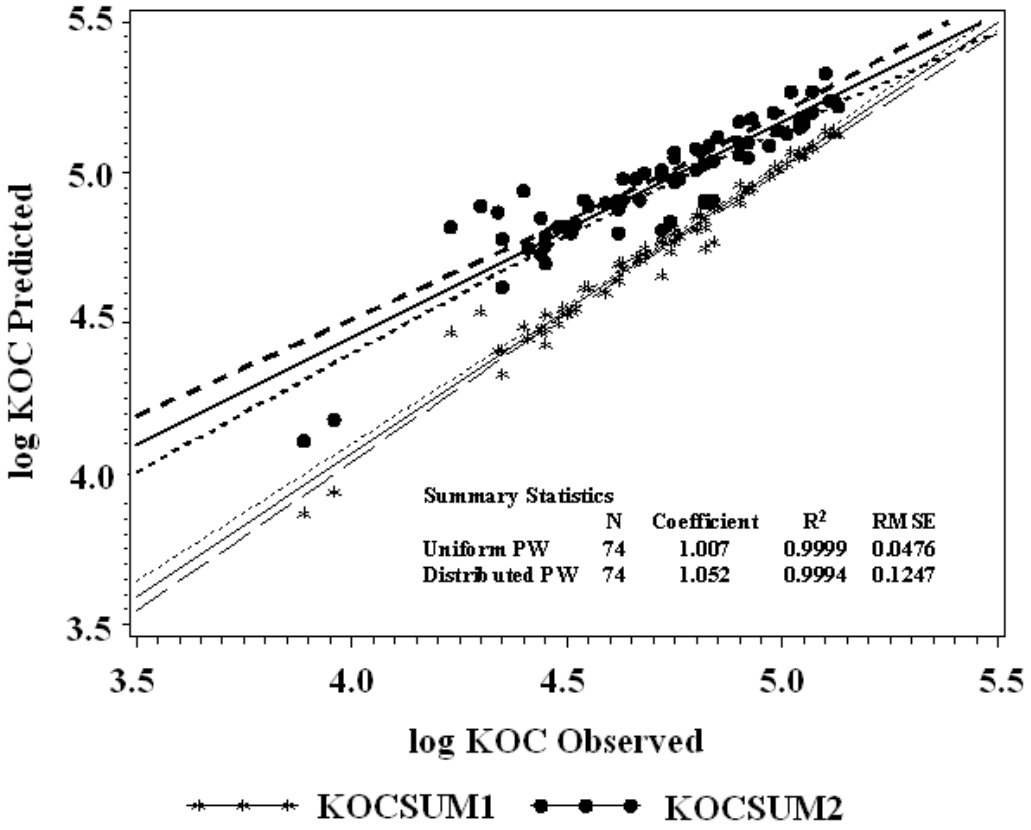

FIGURE 9-2. New Bedford bulk sediment TOC normalized observed distribution coefficient vs. weighted sum of phase specific distribution coefficients (PCBs), with 95 percent confidence intervals.

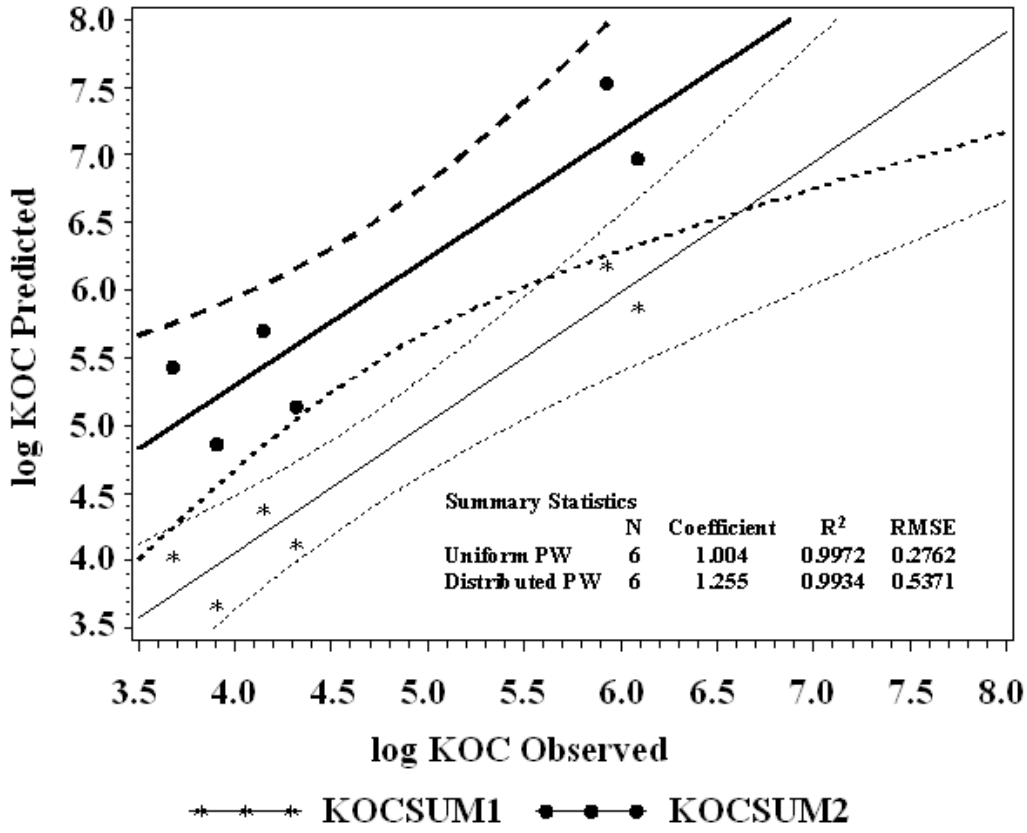

FIGURE 9-3. New York bulk sediment TOC normalized observed distribution coefficient vs. weighted sum of phase specific distribution coefficients (PCBs), with 95 percent confidence intervals.

TABLE 9-1. Log Octanol-Water Partition Coefficient and Mean Theoretical, Observed and Predicted Distribution Coefficients – Equal and Nonuniform Pore Water Assumptions

		Theoretical			Observed		Predicted									
							Uniform Pore Water Assumption					Nonuniform Pore Water Assumption				
Sediment	PCB	K_{OC}	K_{OW}[1]	K_d	K_d	K_{OC}	K_{DOG}	K_{DSOOT}	K_{DOC}	K_{DSUM}	K_{OCSUM}	K_{DOG}	K_{DSOOT}	K_{DOC}	K_{DSUM}	K_{OCSUM}
New Bedford	PCB 7	4.82	5.03	3.13	1.99	3.01	5.35	4.37	4.03	3.3	4.33	5.35	6.06	4.03	3.73	4.75
Calumet	PCB 8	4.82	5.03	3.14	3.61	4.57	5.37	4.63	4.48	3.64	4.6	5.37	6.31	4.48	4.59	5.55
New Bedford	PCB 8	4.82	5.03	3.13	4.06	5.09	6.02	4.28	4.90	4.07	5.1	6.02	5.96	4.90	4.17	5.18
New Bedford	PCB 18	5.14	5.35	3.45	4.05	5.08	6.06	4.34	4.88	4.07	5.09	6.06	6.03	4.88	4.17	5.20
New York[2]	PCB 18	5.14	5.35	3.34	4.81	6.01	7.04	6.37	5.52	4.83	6.03	7.04	8.17	5.52	6.05	7.25
New Bedford	PCB 28	5.34	5.55	3.65	3.98	5.01	5.91	4.2	4.86	4	5.02	5.91	5.89	4.86	4.09	5.11
New Bedford	PCB 40	5.5	5.71	3.81	4.03	5.06	6.04	4.66	4.91	4.08	5.11	6.04	6.34	4.91	4.27	5.29
Calumet	PCB 44	5.58	5.79	3.9	2.83	3.79	4.68	3.75	3.55	2.79	3.75	4.68	5.43	3.55	3.72	4.68
New Bedford	PCB 44	5.58	5.79	3.89	4.06	5.08	6.02	4.37	4.91	4.07	5.1	6.02	6.06	4.91	4.18	5.21
New Bedford	PCB 49	5.68	5.89	3.99	3.94	4.97	6.00	4.2	4.74	3.97	4.99	6.00	5.89	4.74	4.06	5.09
Calumet	PCB 52	5.65	5.86	3.97	3.16	4.11	5.09	3.91	3.95	3.16	4.12	5.09	5.59	3.95	3.91	4.87
New Bedford	PCB 52	5.65	5.86	3.96	4.06	5.08	6.07	4.31	4.88	4.08	5.1	6.07	5.99	4.88	4.17	5.20
New Bedford	PCB 70	5.79	6	4.1	4	5.02	5.99	4.58	4.85	4.03	5.06	5.99	6.27	4.85	4.21	5.23
New Bedford	PCB 82	5.96	6.17	4.27	3.86	4.88	5.82	4.37	4.73	3.88	4.91	5.82	6.05	4.73	4.04	5.06
New Bedford	PCB 87	6.04	6.25	4.35	3.87	4.89	5.81	4.58	4.75	3.9	4.92	5.81	6.27	4.75	4.12	5.15
New Bedford	PCB 97	6.04	6.25	4.35	3.24	4.26	5.47	4.42	4.27	3.48	4.51	5.47	6.11	4.27	3.83	4.85
Calumet	PCB101	6.12	6.33	4.44	3.19	4.15	4.60	4.27	3.96	3.12	4.08	4.60	5.95	3.96	4.22	5.18
New Bedford	PCB101	6.12	6.33	4.43	4.01	5.03	5.99	4.36	4.84	4.02	5.04	5.99	6.05	4.84	4.14	5.16
New York[2]	PCB101	6.12	6.33	4.32	3.04	4.24	5.21	4.54	3.86	3.06	4.25	5.21	6.34	3.86	4.23	5.42
New Bedford	PCB103	5.98	6.19	4.29	3.71	4.73	5.88	4.14	4.18	3.68	4.7	5.88	5.83	4.18	3.83	4.85
New Bedford	PCB114	6.18	6.39	4.49	3.74	4.76	5.78	4.46	4.60	3.8	4.82	5.78	6.15	4.60	4.02	5.04
Calumet[2]	PCB118	6.25	6.46	4.57	2.84	3.8	3.96	3.86	3.64	2.74	3.7	3.96	5.54	3.64	3.82	4.78
New Bedford	PCB118	6.25	6.46	4.56	3.84	4.86	5.83	4.41	4.66	3.85	4.88	5.83	6.1	4.66	4.03	5.06
New Bedford	PCB128	6.42	6.63	4.73	3.69	4.71	5.71	4.49	4.59	3.76	4.78	5.71	6.18	4.59	4.01	5.03
New Bedford	PCB136	5.98	6.19	4.29	3.84	4.87	5.86	4.53	4.71	3.9	4.92	5.86	6.21	4.71	4.10	5.13
New Bedford	PCB137	6.5	6.71	4.81	3.74	4.77	5.83	4.43	4.54	3.79	4.81	5.83	6.12	4.54	4.00	5.02
New Bedford	PCB138	6.5	6.71	4.81	3.69	4.71	5.71	4.51	4.56	3.74	4.77	5.71	6.2	4.56	4.01	5.03
New Bedford	PCB141	6.5	6.71	4.81	3.76	4.78	5.78	3.96	4.53	3.75	4.78	5.78	5.65	4.53	3.84	4.87
New Bedford	PCB151	6.34	6.55	4.65	3.8	4.83	5.94	4.31	4.50	3.83	4.85	5.94	6	4.50	3.98	5.01
New Bedford	PCB156	6.63	6.84	4.94	3.68	4.71	5.85	4.35	4.40	3.73	4.75	5.85	6.03	4.40	3.93	4.95
New Bedford	PCB167	6.71	6.92	5.02	3.69	4.72	5.74	4.31	4.50	3.72	4.75	5.74	6	4.50	3.91	4.94
New Bedford	PCB170	6.88	7.09	5.19	3.67	4.69	5.74	4.36	4.45	3.7	4.72	5.74	6.04	4.45	3.91	4.94
New Bedford	PCB180	6.96	7.17	5.27	3.45	4.47	5.48	4.23	4.27	3.48	4.51	5.48	5.92	4.27	3.74	4.76
New Bedford	PCB183	6.82	7.03	5.13	3.49	4.52	5.51	4.33	4.38	3.56	4.58	5.51	6.02	4.38	3.82	4.85
New Bedford	PCB185	6.74	6.95	5.05	3.56	4.59	5.65	4.44	4.41	3.63	4.66	5.65	6.13	4.41	3.91	4.94
New Bedford	PCB191	6.96	7.17	5.27	3.74	4.77	5.75	4.1	4.42	3.68	4.71	5.75	5.78	4.42	3.82	4.84
New Bedford	PCB194	7.34	7.55	5.65	2.9	3.93	4.85	3.59	3.69	2.88	3.9	4.85	5.28	3.69	3.11	4.14
New Bedford	PCB195	7.13	7.34	5.44	3.37	4.39	5.37	4.39	4.23	3.42	4.44	5.37	6.08	4.23	3.78	4.81
New Bedford	PCB196	7.2	7.41	5.51	3.43	4.45	5.46	4.29	4.25	3.46	4.49	5.46	5.98	4.25	3.75	4.78
New Bedford[2]	PCB199	6.82	7.03	5.13	3.68	4.7	5.75	4.47	4.51	3.73	4.76	5.75	6.16	4.51	3.98	5.01
New Bedford	PCB201	7.18	7.39	5.49	3.46	4.48	5.45	4.29	4.31	3.49	4.51	5.45	5.98	4.31	3.77	4.79
New Bedford	PCB203	7.2	7.41	5.51	3.34	4.37	5.40	4.54	4.21	3.42	4.45	5.40	6.23	4.21	3.88	4.90
New Bedford	PCB206	7.59	7.8	5.9	3.51	4.53	5.63	4.37	4.20	3.53	4.55	5.63	6.06	4.20	3.83	4.85
New Bedford[2]	PCB207	7.28	7.49	5.59	3.51	4.54	5.70	4.29	4.18	3.56	4.58	5.70	5.98	4.18	3.81	4.83
Calumet	PCB208	7.26	7.47	5.58	2.48	3.44	4.26	3.17	3.30	2.45	3.41	4.26	4.85	3.30	3.18	4.13
New Bedford	PCB208	7.26	7.47	5.57	3.37	4.4	5.43	4.16	4.07	3.36	4.38	5.43	5.85	4.07	3.63	4.66
New York	PCB208	7.26	7.47	5.46	2.6	3.79	4.91	4.28	3.13	2.65	3.85	4.91	6.07	3.13	3.95	5.15

[1] Hansen et al. 1999. [2] Distribution coefficients calculated with estimated pore water concentration (flagged J values).

Labile and Desorption Resistant Fraction - Coefficient Comparisons. The ratio of the predicted organic carbon coefficient to organic carbon normalized coefficient for the available fraction were compared to assess the validity of the assumptions regarding labile phases for the study sediments. Similarly, the ratio of the predicted soot coefficient was compared to the coefficient for the desorption resistant fraction to assess the validity of the assumptions regarding the desorption resistant phase for the study sediments.

The ratio of the available fraction distribution coefficient to the observed organic carbon normalized coefficient ($K_{OC, Avail}$ /$K_{OC, Obs}$) ranged from 0.64 to 0.89, with a mean of 0.75 (Table 9-2). For the uniform pore water concentration assumption, the mean ratio of the OC coefficient to the coefficient for the available fraction ($K_{d,OC}$ /$K_{OC, Avail}$) was 1.29, ranging from 1.03 to 1.52. Also for uniform pore water assumption, the mean ratio of the combined coefficient for organic carbon and oil and grease to available fraction coefficient ($K_{d, OCOG}$/$K_{OC, Avail}$) was 1.35, ranging from 1.11 to 1.58. These ratios were unchanged for the nonuniform pore water concentration.

For the uniform pore water assumption, the ratio of predicted $K_{d,soot}$ to the coefficient for the resistant fraction ($K_{d, Resist}$) ranged from 0.83 to 1.05, with a mean of 0.94. The soot coefficient was less than the coefficient for the desorption resistant fraction for 11 of 16 compounds. For the nonuniform pore water assumption, however, the soot coefficient is greater than the coefficient for the desorption resistant fraction in all cases, with a mean ratio of 1.3, ranging from 1.16 to 1.45. Coefficients obtained with the uniform pore water assumption suggest some of the desorption resistant phases may lie in the OG or OC fractions, while the coefficients obtained with the nonuniform pore water assumption suggest that the soot may account for all of the desorption resistant fraction as well as some of the labile fraction.

The relative magnitude of soot and OC coefficients for the uniform pore water assumption suggests that soot is not as important to PCB sorption as to PAH sorption. However, for the nonuniform pore water assumption, the soot coefficient is consistently greater than the OC coefficient for both PAHs (Chapter 8) and PCBs, with a mean difference of 1.96- and 1.63-log units, respectively.

Soot Coefficient Comparisons to Literature Values. As for PAHs, a wide range of values was found for PCB sorption to black carbon in the literature (Table 9-3). There were relatively few published coefficients obtained on natural sediments, however, and those available were based on sorption studies, rather than direct measurement of the insitu contaminant levels and sorptive phases. Only one reference (Cornelissen et al. 2004a) reported any values for "native" compounds, and these were limited to PAHs. The environmental coefficients reported by Cornelissen et al. (2004a) for PCBs, however, represent values obtained by sorption studies on sediment in the presence of natural organic material and are considered to be the most representative reference values available.

As was done for PAHs in Chapter 8 (Figures 8-10 to 8-12), predicted log K_{dSoot} (nonuniform pore water) and reference values from Table 9-3 were plotted against log K_{ow} for PCBs measured. Calumet coefficients are fairly well bracketed by reference values except above log K_{ow} 6.5, where the predicted coefficients and reference values begin to diverge due to inverse slopes (Figure 9-4). The negative trend displayed by the predicted coefficients is also seen for the observed bulk sediment K_d for Calumet. New Bedford values are also well bracketed by reference values, but display virtually no correlation to log K_{ow} values (Figure 9-5). Observed bulk sediment K_d mimics this trend, although this is in part due to the influence of the very small coefficient that was obtained for PCB 7 (log K_{dSoot} 1.99). When this point is eliminated from the

TABLE 9-2. Labile and Desorption Resistant Fraction Distribution Coefficients Compared to Predicted Phase Specific Distribution Coefficients - PCBs

			Bulk Sediment log Koc			log K_{dOC}	log $K_{dOC\&OG}$	log K_{dSOOT}			
Compound	**Reference**	**Sediment**	**Theoretical**	**Obs**	**Mean Labile**	**Mean Predicted**	**Mean Predicted**	**Mean Predicted[1]**		**Desorption Resistant Fraction**	**Desorption Resistant Fraction**
PCB 3	Cornelissen et al. 2004	Lake Ketelmeer		5.22							
PCB 4	Cornelissen et al. 2004	Lake Ketelmeer		4.37							
PCB 8	This Study	Calumet	4.82	4.57	3.41	4.48	4.6	4.63	6.31	4.6	0.93
PCB 8	This Study	New Bedford	4.82	5.09	4.17	4.9	5.11	4.28	5.96	5.14	0.878
PCB 18	This Study	New Bedford	5.14	5.08	0	4.88	5.11	4.34	6.03	5.08	1
PCB 18	This Study	New York	5.14	6.01	5.37	5.52	5.96	6.37	8.17	6.1	0.773
PCB 28	This Study	New Bedford	5.34	5.01	0	4.86	5.04	4.2	5.89	5.01	1
PCB 40	This Study	New Bedford	5.5	5.06	0	4.91	5.12	4.66	6.34	5.06	1
PCB 44	This Study	Calumet	5.58	3.79	2.47	3.55	3.75	3.75	5.43	3.81	0.952
PCB 44	This Study	New Bedford	5.58	5.08	4.09	4.91	5.11	4.37	6.06	5.12	0.898
PCB 49	This Study	New Bedford	5.68	4.97	0	4.74	5	4.2	5.89	4.97	1
PCB 52	This Study	Calumet	5.65	4.11	2.8	3.95	4.15	3.91	5.59	4.14	0.951
PCB 52	This Study	New Bedford	5.65	5.08	0	4.88	5.11	4.31	5.99	5.08	1
PCB 70	This Study	New Bedford	5.79	5.02	4.04	4.85	5.07	4.58	6.27	5.07	0.897
PCB 82	This Study	New Bedford	5.96	4.88	3.11	4.73	4.92	4.37	6.05	4.89	0.983
PCB 87	This Study	New Bedford	6.04	4.89	0	4.75	4.93	4.58	6.27	4.89	1
PCB 97	This Study	New Bedford	6.04	4.26	0	4.27	4.51	4.42	6.11	4.26	1
PCB101	This Study	Calumet	6.12	4.15	3.1	3.96	4.02	4.27	5.95	4.18	0.91
PCB101	This Study	New Bedford	6.12	5.03	3.83	4.84	5.06	4.36	6.05	5.06	0.937
PCB101	This Study	New York	6.12	4.24	0	3.86	4.2	4.54	6.34	4.24	1
PCB103	This Study	New Bedford	5.98	4.73	0	4.18	4.71	4.14	5.83	4.73	1
PCB114	This Study	New Bedford	6.18	4.76	0	4.6	4.83	4.46	6.15	4.76	1
PCB118	This Study	Calumet	6.25	3.80	2.76	3.64	3.66	3.86	5.54	3.84	0.908
PCB118	This Study	New Bedford	6.25	4.86	3.79	4.66	4.89	4.41	6.1	4.9	0.915
PCB128	This Study	New Bedford	6.42	4.71	0	4.59	4.79	4.49	6.18	4.71	1
PCB138	This Study	New Bedford	6.5	4.71	3.18	4.56	4.77	4.51	6.2	4.73	0.971
PCB141	This Study	New Bedford	6.5	4.78	0	4.53	4.79	3.96	5.65	4.78	1
PCB151	This Study	New Bedford	6.34	4.83	3.36	4.5	4.86	4.31	6	4.84	0.966
PCB153	Karikhoff 1981	Unspecified	6.43	5.62							
PCB155	Karikhoff 1981	Unspecified	5.95	6.08							
PCB167	This Study	New Bedford	6.71	4.72	0	4.5	4.75	4.31	6	4.72	1
PCB170	This Study	New Bedford	6.88	4.69	0	4.45	4.73	4.36	6.04	4.69	1
PCB180	This Study	New Bedford	6.96	4.47	0	4.27	4.51	4.23	5.92	4.47	1
PCB183	This Study	New Bedford	6.82	4.52	0	4.38	4.59	4.33	6.02	4.52	1
PCB185	This Study	New Bedford	6.74	4.59	3.99	4.41	4.66	4.44	6.13	4.68	0.749
PCB194	This Study	New Bedford	7.34	3.93	0	3.69	3.91	3.59	5.28	3.93	1
PCB195	This Study	New Bedford	7.13	4.39	0	4.23	4.45	4.39	6.08	4.39	1
PCB196	This Study	New Bedford	7.2	4.45	0	4.25	4.49	4.29	5.98	4.45	1
PCB199	This Study	New Bedford	6.82	4.7	3.21	4.51	4.77	4.47	6.16	4.72	0.968
PCB201	This Study	New Bedford	7.18	4.48	0	4.31	4.52	4.29	5.98	4.48	1
PCB203	This Study	New Bedford	7.2	4.37	0	4.21	4.45	4.54	6.23	4.37	1
PCB206	This Study	New Bedford	7.59	4.53	0	4.2	4.56	4.37	6.06	4.53	1
PCB208	This Study	New Bedford	7.26	4.4	0	4.07	4.39	4.16	5.85	4.4	1
PCB208	This Study	New York	7.26	3.79	0	3.13	3.75	4.28	6.07	3.79	1

[1] First value based on uniform pore water assumption; second value based on nonuniform pore water assumption.

TABLE 9-3. Mean Predicted log K_dSoot for Study Sediments and Published Distribution Coefficients for Other Sediments and Standard Reference Materials – PCBs

| | | Homolog Groups/Congeners | | |

plot of observed K_d, the trendline exhibits a negative slope ($y = -0.315x + 5.78$, $R^2 = 0.648$). There were only three PCB coefficients obtained for the New York sediment, but these also display a negative slope when plotted against log K_{ow} (Figure 9-6). This is the opposite of the trend displayed by log K_{dSoot} values obtained for PAHs for this sediment (Figure 8-12). The center value (PCB 101) is well within the range of the reference values. The first value (PCB 18) is roughly two orders of magnitude higher than the largest reference value. There were no reference values for the last point (PCB 208) but if observed trends were consistent, it would appear to be within an order of magnitude of expected values. The plot of the New York bulk sediment K_d for PCBs also displays a negative trend (Figure 9-6). Of the Lake Ketelmeer reference values (Cornelissen 2004a), the only one with multiple data points also displayed a negative correspondence to log K_{ow}.

Although the thermodynamically derived values reported in Table 9-3 (van Noort 2003) suggest a general trend of increasing coefficients with increasing K_{ow}, similar contradictions exist there as well. The coefficient reported for PCB 54, for example, was lower than the value for PCB 19, despite a 0.16-log larger K_{ow}. Modeled values were developed based on free energy differences rather than K_{ow}, however (van Noort 2003). Thermodynamic models also presume conditions such as monolayer sorption that are not necessarily met in the natural environment. Competitive sorption is not taken into consideration. Under those circumstances, deviations from values derived solely from sorbate properties are certainly possible and reflect the complexity of the true interactions between sorbate and sorbent in the environment. It is possible that differences in hydrophobicity have less impact on PCB sorption than steric effects. More highly chlorinated PCBs also have greater surface area. Sorption may therefore be inhibited for these compounds, resulting in distribution coefficients of similar magnitude to those obtained for smaller, but less hydrophobic PCBs.

OG Coefficient Comparisons to Literature Values. Distribution of hydrophobic organic contaminants to the oil and grease phase has not been widely studied. A study conducted by Jonker et al. (2003) on PAH partitioning to sediments spiked with different oils was presented in Chapter 8. A more recent study (McNamara et al. 2005) examined the respective partitioning of PCBs to oil in the presence of natural organic matter. Distribution coefficients for partitioning to the oil phase were not given, but the authors concluded that partitioning of the PCBs to the oil exceeded partitioning to the OC by an order of magnitude. This is consistent with the relative magnitude of the OG and OC distribution coefficients obtained in the present study for PCBs.

DISCUSSION

Soot partition coefficients reported by Jonker and Koelmans (2002) for PCBs were for materials that had been thoroughly washed to remove floating and easily soluble fractions, then dried, ground and passed through a 50 μm sieve. The intent was to produce a small particle fraction representative of materials subject to atmospheric transport. Because black carbon sorption is thought to be a surface area dependent phenomenon (Cornelissen et al. 2004a), large differences in surface area between the black carbon in the study sediments and other sediments or reference values could account for substantial disparity in coefficient values. In all three study sediments, the highest soot concentrations were found in the sand fraction (>75 μm particles), with the next highest concentrations in the silt fraction (5 -75 μm). Because these materials are

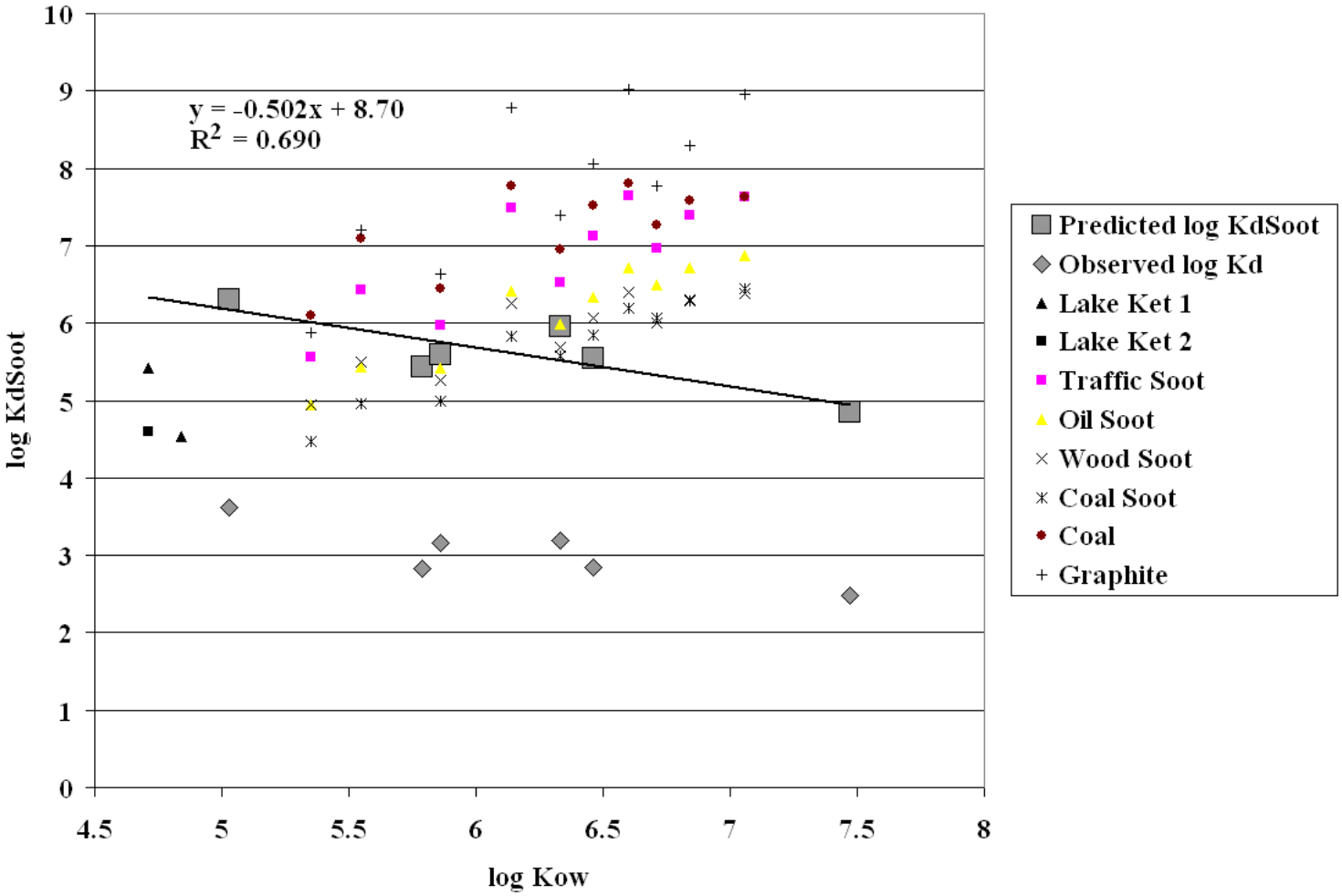

FIGURE 9-4. Calumet predicted log K_{dSoot} and available reference values vs. PCB log K_{ow}.

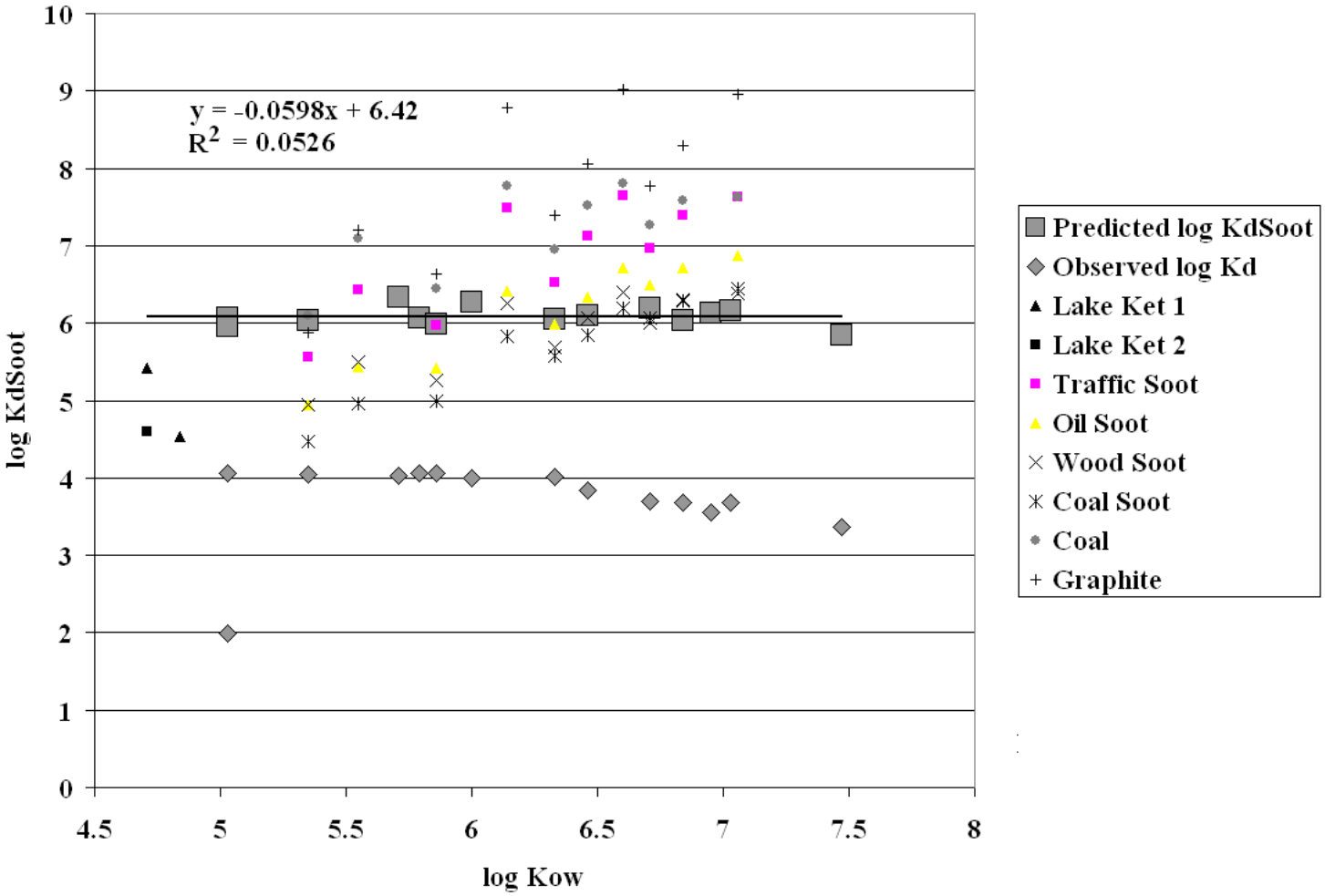

FIGURE 9-5. New Bedford predicted log K_{dSoot} and available reference values vs. PCB log K_{ow}.

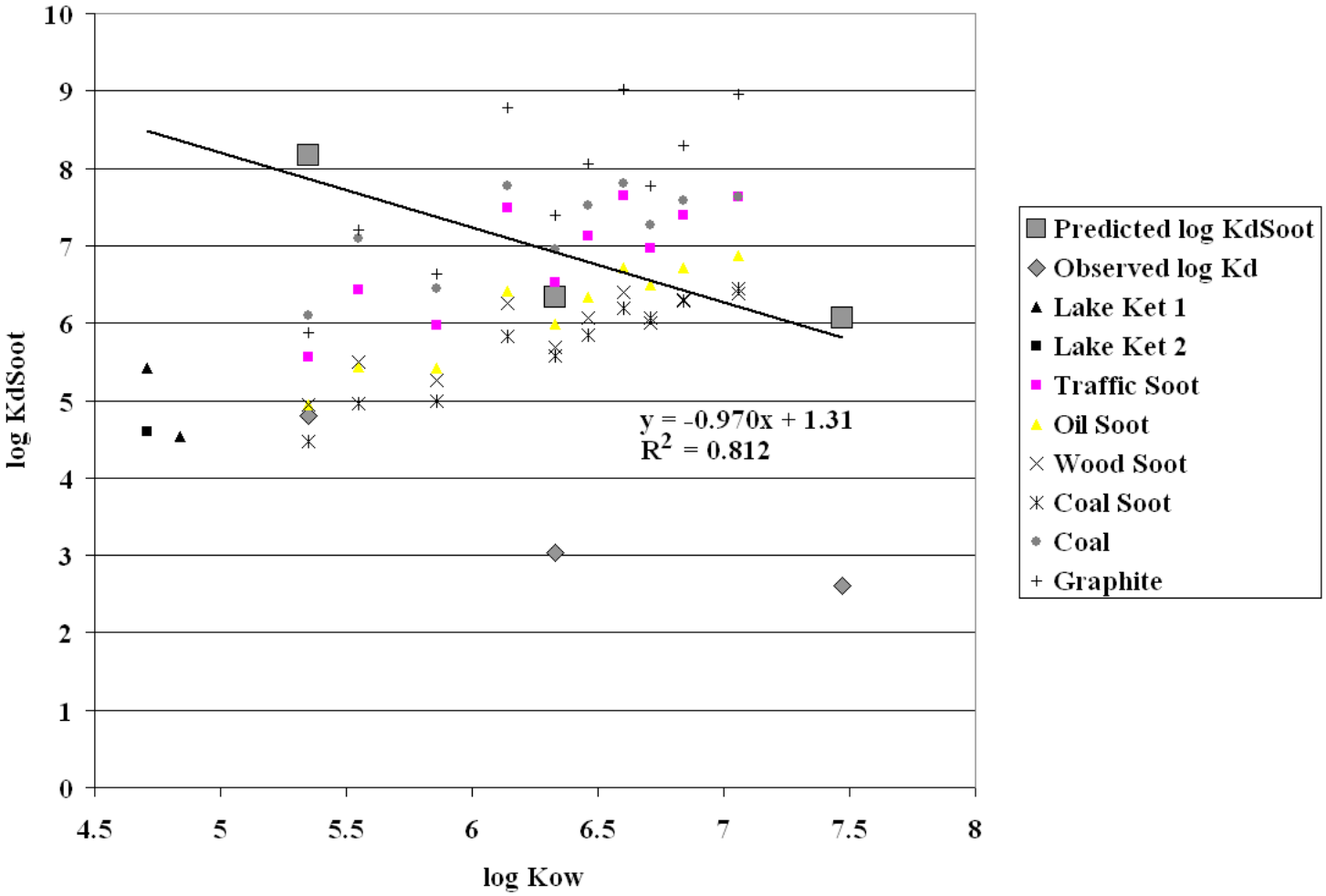

FIGURE 9-6. New York predicted log K_{dSoot} and available reference values vs. PCB log K_{ow}.

predominantly coarser than those utilized in Jonker and Koelmans (2002), they would be expected to have lower surface area and correspondingly lower distribution coefficients. PCB coefficients were on average from 0.02 log units (New York) to 0.3 log units (Calumet and New Bedford) lower than those reported by Jonker and Koelmans (2002).

Effects of competition from naturally occurring organic materials must also be considered in comparing the reported literature values to the results obtained for the study sediments. Cornelissen et al. (2004a) reported two Freundlich coefficient values obtained from isotherm studies on natural sediments: an intrinsic and an environmental value. The intrinsic value was obtained from sediment combusted to remove natural organic material. The environmental value was derived from isotherms for the un-combusted sediment (giving $K_{F,TOC}$) and from the intrinisic coefficient ($K_{BC,int}$). Two PCBs were studied (PCB 3 and PCB 4). The environmental black carbon coefficient ($K_{BC,env}$) was estimated to be a factor of 7 smaller than the intrinsic value for PCB 3. A similar relationship was also noted for PAHs, and suggests that distribution coefficients obtained on natural sediments may reasonably be expected to be substantially smaller than intrinsic values due to competition from natural organic materials.

The environmental BC coefficients reported by Cornelissen et al. (2004a) are considered to be most comparable to the study sediments, of those reported in Table 9-3, and are in generally good agreement with the soot coefficients reported here. Cornelissen et al. (2004a) also observed reduced sorption of non-planar PCB 4, as compared to planar PAHs, but comparable trends were not consistently reflected in the respective soot coefficients obtained for PCBs in this study. For the study sediments, all but 13 of 37 non-planar PCBs distributed in higher proportions to the OC than to the soot, but only 3 of 10 planar PCBs distributed preferentially to the soot over the OC. A possible explanation is that preference does not equate to selectivity. That is, both planar and non-planar PCBs will sorb to either soot or OC, depending upon which phase is first encountered. Sites favorable to sorption of non planar PCBs may be more limited for soot, however, or large PCBs may occlude multiple sorption sites, and concentrations in this phase are therefore typically lower than those seen for OC. Higher concentrations of planar PCBs in organic carbon can possibly be explained simply by accessibility. Given the relative abundance of OC, the likelihood of encountering OC in the matrix is greater than the likelihood of encountering soot.

SUMMARY AND CONCLUSIONS

As was seen for PAHs, good correspondence was obtained between observed K_d and the composite coefficient obtained using the predicted phase specific coefficients and a uniform pore water concentration for calculation of each coefficient. Also consistent with the results obtained for PAHs, PCB coefficients obtained using a nonuniform pore water concentration were approximately an order of magnitude higher for the soot phase while coefficients for OG and OC were not greatly affected by the pore water assumptions.

Coefficients obtained with the uniform pore water assumption suggest some of the desorption resistant phases may lie in the OG or OC fractions, based on comparison to coefficients for labile phases. Coefficients obtained with the nonuniform pore water assumption, however, suggest that the soot may account for all of the desorption resistant fraction as well as some of the labile fraction.

The relative magnitude of soot and OC coefficients for the uniform pore water assumption suggests that soot is not as important to PCB sorption as observed for PAH sorption. However, for the nonuniform pore water assumption, the PCBs soot coefficient is consistently greater than the OC coefficient, with a mean difference of 1.63-log units. The relative magnitude of the K_{dSoot} for PCBs, as compared to PAHs, also suggests that soot is not as important in PCB sorption as in PAH sorption, particularly for Calumet and New Bedford. K_{dSoot} coefficients were more comparable for PCBs and PAHs for the New York sediment, perhaps reflecting the differences in grain size and, consequently, surface area of the soot for this fine sediment.

Soot distribution coefficients obtained for the study sediments based on the uniform pore water concentration were in many cases lower than published distribution coefficients for standard reference materials, although largely within the order of magnitude difference observed by other researchers for intrinisic versus environmental sorption. Differences between predicted and reported black carbon coefficients may be attributable to the effects of competition for sorption sites on the black carbon in natural sediments and to differences in type and size of black carbon in the study sediments relative to materials used in reported studies. Relatively good correspondence to reported values for environmental black carbon sorption in natural sediments was observed. Coefficients obtained using nonuniform pore water concentrations were comparable to the intrinsic values reported for carbon phases representative of those expected in natural urban sediments. This is also consistent with the assertion that intrinsic and environmental coefficients are algebraically different, and that this may account for a large part of the observed differences between them.

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CHAPTER 10

OVERVIEW, GENERAL OBSERVATIONS AND CONCLUSIONS

OVERVIEW

Fractionation studies were conducted on three natural sediments to obtain differential measurements of contaminant concentrations and sorptive phases. The major objectives of this research effort were to 1) ascertain the distribution of PAHs and PCBs in the study sediments with respect to operationally defined size and density fractions, 2) evaluate the correlation between contaminant distribution and distinct sorptive phases, 3) from the correlations, develop a model for phase specific distribution coefficients, and 4) assess the utility of fractionation studies to treatment and fate and effects evaluations. The study consisted of three major elements:

Literature Review. Literature was reviewed to identify relevant PCB and PAH characteristics and applicable sorption theory and research. Recent findings with respect to contaminant partitioning were reviewed and the implications and relevance to the present study assessed.

Review of the literature suggests that this study is relatively unique in several respects. Contaminant distribution between sorptive phases was obtained by direct correlation of the contaminant mass and the mass of multiple sorptive phases (oil and grease, soot, organic carbon and clay). The suite of analytes was quite large, including 70 PCBs and 17 PAHs, in addition to the sorptive phases. With replication, the resulting data set provided sufficient data points to facilitate statistical analysis and establish trends. Results reflect contaminant distribution occurring in the presence of multiple sorptive phases and competing sorbates, conditions not reflected by most reference values reported in the literature.

Size and Density Fractionation Study. Partitioning of PCBs and PAHs in sediments was assessed as a function of sediment composition. Operationally defined size and density fractions were isolated and analyzed for direct measurement of contaminants within those fractions and visualization of distribution trends. The importance of distribution trends to treatability using separation was evaluated.

The fractionation procedures used were the end product of earlier efforts to develop simple bench scale procedures suitable to apriori evaluation of physical separation treatability. The fractionation study consisted of separating the bulk sediment into size and density fractions representative of fractions that can readily be separated with simple gravimetric equipment, and fractions most likely to be contaminant laden. Soil size fractions are very specifically delineated in a number of well-established classification systems. Under those systems, sand, silt and clay classification refer not only to specific particle sizes, but also imply certain material properties reflecting mineralogical differences, such as the plasticity associated with clay minerals. For the purposes of this study, however, sand, silt and clay fractions were operationally defined as follows, and included both mineral and organic materials reporting to those fractions. Sand was obtained by wet sieving the bulk sediment on a 200-mesh sieve. Particles >4.75mm were first removed, thus defining the sand fraction as particles between 75 μm and 4.75 mm (consistent

with the USCS size classification). The slurry passing the 200-mesh sieve (<75 μm particles) was processed through a 2-inch hydrocyclone, producing the silt and clay fractions. The underflow was classified as the silt fraction, and the overflow as the clay fraction. Although the process streams produced in this manner demonstrate considerable overlap in particle size, they do differ in the relative amount of silt (5-75 μm) and clay (< 5 μm) particles they contain. The process served to produce one fraction enriched in silt and another enriched in clay, rather than a pure silt or pure clay fraction. Such a separation is more representative of practical applications than alternative methods of separation, and produced sample fractions of sufficiently different properties, and in sufficient volume, to assess the impact of clay content on contaminant distribution.

Density separations were designed to separate organic and mineral fractions. Separation was made at a specific gravity of 2.0 using heavy media. This is a sufficiently high density to capture most soot material in the organic fraction, while excluding most minerals. Some clay was probably entrapped in the organic fraction due to the fact that clay tends to adhere to larger particles, and the fluid viscosity might prevent efficient movement of such small particles. Also, measurable quantities of soot were found in the mineral fraction. These findings reflect the difficulty of capturing the entire continuum of any of the sorptive phases. The potential utility of fractionation studies is in facilitating assessment of contaminant distribution between these phases by obtaining differential measurements of contaminants and sorptive phases.

Modeling. The relationship between contaminant concentration and sorptive phases was evaluated through regression of the fractionation data. A best-fit model was selected and, from this, phase specific distribution coefficients were developed. Overall findings were compared to those reported by other researchers and implications with respect to hydrophobicity, steric effects, competitive sorption and desorption resistance were discussed.

Contaminant mass associated with each of the sorptive phases was obtained by regression on the fractionation data for several models. The two linear models were:

$$M_i = b_1 M_{OG} + b_2 M_{SOOT} + b_3 M_{OC} \quad (10\text{-}1)$$

$$M_i = b_1 M_{OG} + b_2 M_{SOOT} + b_3 M_{OC} + b_4 M_{CLAY} \quad (10\text{-}2)$$

where

M_i = the mass of contaminant i in the bulk sediment, size fraction or density fraction
M_{OG}, M_{SOOT}, M_{OC}, M_{CLAY} = mass of the sorptive phases in the bulk sediment or size or density fractions
b_1, b_2, b_3, b_4 = concentration of contaminant i associated with the specific phase

Linear regression was performed on the model $M_{i\ Predicted} = M_{i\ Measured}$, to evaluate the correspondence of the modeled to measured values. A paired t test was used to assess the equality of the predicted and measured values individually. Normality of the difference values was first evaluated with the Shapiro-Wilke test to determine suitability of the t test. Contaminant mass predicted for the sorptive phases by the model were then tabulated and plotted against the measured contaminant mass in the bulk sediment. Improvement in model fit with inclusion of the clay fraction in the model was assessed with an F test.

Distribution coefficients were developed from the regression data. Values were calculated using a uniform pore water concentration (assuming each phase was in equilibrium with the pore water at the measured concentration) and also using a nonuniform pore water concentration (assuming the dissolved concentration was largely attributable to the labile phases). The weighted sum of the phase specific distribution coefficients from both methods were compared to the observed bulk sediment coefficient, and to coefficient values reported in the literature for soot, black carbon free organic carbon, and organic carbon normalized bulk sediment coefficients.

GENERAL OBSERVATIONS

Contaminant and Sorptive Phase Distribution. Both clay and organic fractions appear to be important to PAH and PCB sorption for these sediments. For PAHs, organic sorption appears to dominate, although predicted clay concentrations were comparable to organic carbon concentrations for the New Bedford sediment. For the other sediments, concentrations in the organic fraction were roughly an order of magnitude higher than in the clay fraction. For PCBs mass distribution to the mineral phase was consistently greater than for PAHs, for all three sediments. This was thought to be attributable to the influence of the clay minerals present in the mineral fraction. There are, however, components of all the sorptive phases in each of the size and density fractions, attributable to the natural variation in physical properties of each of these phases, as well as inherent inefficiencies in the separation processes. This makes discriminating between the influence of the different phases in each fraction difficult without statistical analysis.

An expression for residual contaminant concentration resulting from removal of a selected size or density fraction was developed:

$$C_F = C_I * \left(\frac{1 - f_i}{1 - f_{sed}} \right) \tag{10-3}$$

where

f_i = fraction contaminant mass in size or density fraction removed
f_{sed} = fraction of sediment mass comprised by size or density fraction removed
C_I = contaminant concentration in bulk sediment, µg/kg
C_F = contaminant concentration in treated sediment, µg/kg

In addition, an expression for the percent reduction (R) in contaminant concentration was developed:

$$R = \left(1 - \left(\frac{1 - f_i}{1 - f_{sed}} \right) * 100 \right) \tag{10-4}$$

Based on application of these relationships to the study sediments, it is apparent that achieving reduction of contaminant concentrations by selective separation is dependent upon a favorable contaminant to sediment mass ratio in the fraction removed. If the sediment mass of the targeted fraction is large relative to the contaminant mass in that fraction, concentration in the remaining materials may be higher after separation, rather than lower. This illustrates the value of fractionation data to feasibility analysis for separation as this breakpoint concentration can be identified based on bench scale testing. The proportion and character of materials reporting to the process streams can be assessed and sediment and contaminant mass balance constructed. An appropriate target fraction can be identified, and the processes and equipment selected on the basis of the specific requirements for effective separation of that fraction from the bulk sediment.

Correlations. The mass of contaminant associated with each of the sorptive phases was determined by regression. This is typically problematic with fractionation data which appears, in part, to be attributable to violation of some of the inherent assumptions of ordinary linear regression. Environmental data is often not normally distributed, and collinearity of variables can interfere with regression. Further, variability of the data may be large enough to obscure the trends the analysis is intended to identify, particularly if the relative magnitude of the independent variables is very disparate.

Collinearity is probably unavoidable in data obtained from navigation sediments. This may be due to analytical limitations (nested measurements of organic carbon and carbon content contributed by contaminants, for example), similarity in causative agents (sorptive phases deriving from the same source may demonstrate corresponding variations in magnitude even in the absence of true interdependence), or to sorption between the sorptive phases themselves. In this study, TOC was first adjusted for soot and then for oil and grease (oil and grease concentration was deducted from the non-soot TOC values), but no adjustment was made for contaminant-contributed carbon. This is a data conditioning step that deserves further evaluation, however.

The ENTROPY procedure in SAS is robust to problems such as collinearity, and was used to successfully obtain estimates of contaminant mass associated with each of the sorptive phases. The procedure essentially allows some bias in order to reduce variance. Coefficients can be constrained to positive values, eliminating the problem of physically meaningless (in this case, negative) coefficients.

There was some evidence (based on the F test) that clay is a statistically significant sorptive phase in the Calumet sediment, particularly for PCBs. This was only true for a few compounds for New Bedford and New York, however. The model that was consistently significant for all compounds for all three sediments included three sorptive phases, oil and grease, soot and (black carbon free) organic carbon:

$$M_i = b_1 M_{OG} + b_2 M_{SOOT} + b_3 M_{OC} \qquad (10\text{-}5)$$

Model coefficients for the three variable model (Equation 10-5) were obtained using all of the sediment data (bulk sediment and size and density fractions) and produced very good correspondence to observed sediment mass in the bulk sediment (Figure 10-1). Correspondence to the different fractions was more variable (Figure 10-2). This is thought to be attributable largely to the magnitude of the bulk sediment concentrations as compared to the concentration in the fractions. Concentrations in the bulk sediment reflect the central tendency of the data,

contaminant concentrations in the fractions being generally much higher or much lower. Because linear regression is essentially a determination of central tendency, predicted values would therefore be expected to be more representative of the bulk sediment than of the fractions. This would appear to diminish the predictive value of regression on fractionation data for process streams, however. The error with respect to the size and density fractions is relatively large in some cases. Better results for the fractions might be obtained by grouping the data within more limited concentration ranges, however, and is another area identified for further inquiry.

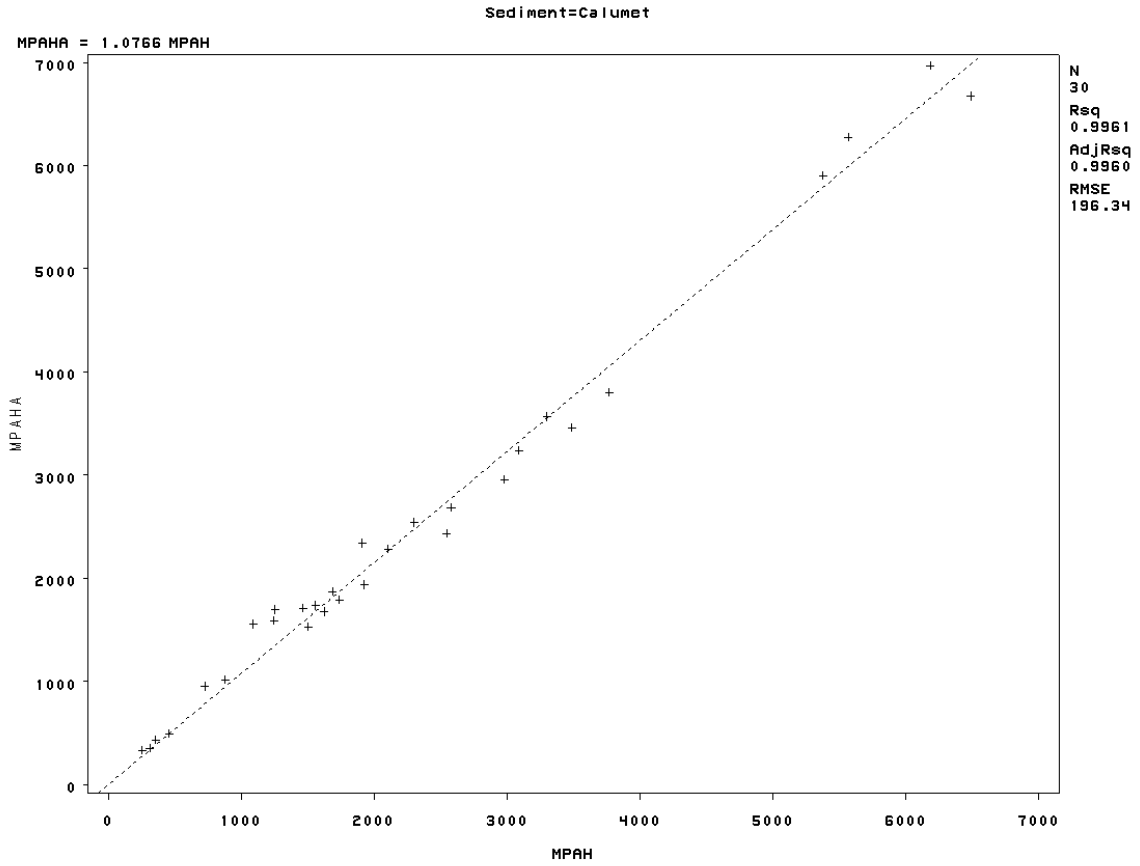

FIGURE 10-1. Calumet predicted PAH mass versus measured PAH mass in bulk sediment.

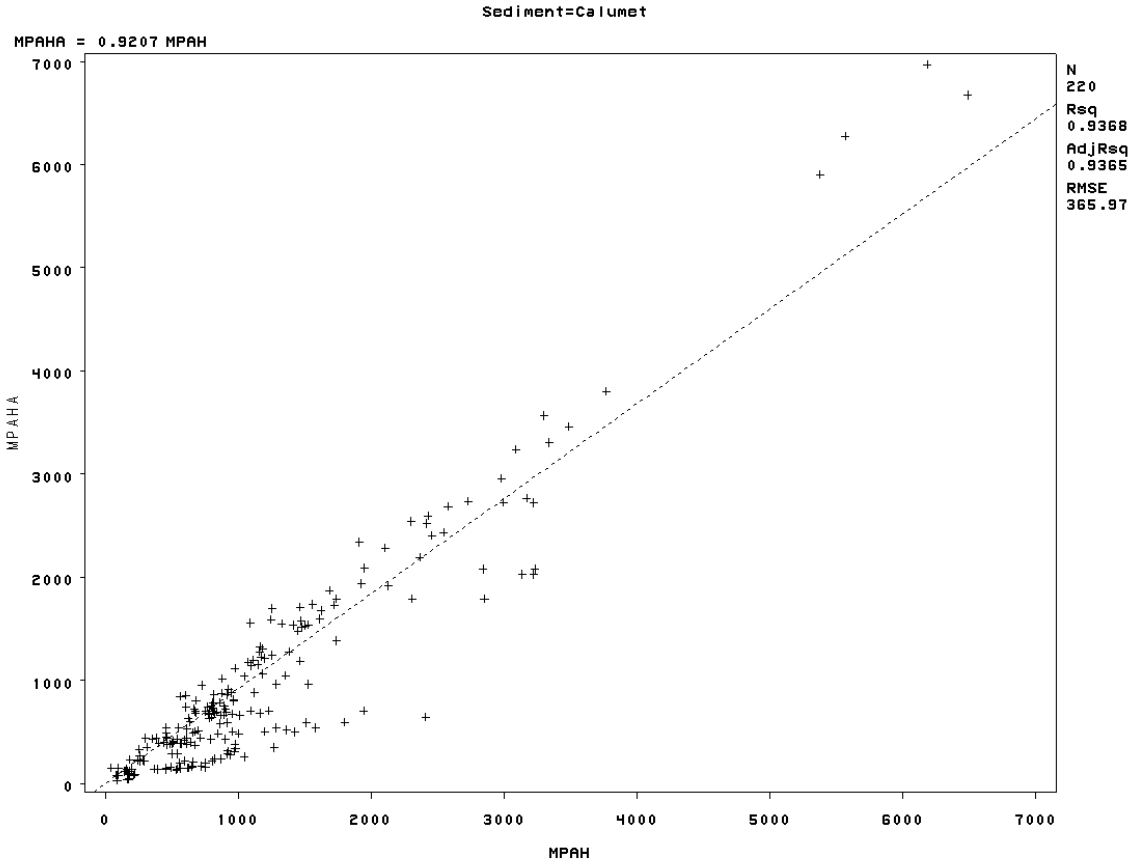

FIGURE 10-2. Calumet predicted PAH mass versus measured PAH mass in bulk sediment and size and density fractions.

Distribution Coefficients. Distribution coefficients obtained using a uniform pore water concentration corresponded very well with observed coefficients for the bulk sediment data. Distribution coefficients obtained using a nonuniform pore water concentration, based on the assumption that soot associated contaminants are desorption resistant, exceed observed coefficients by 0.11- to 1.37-log units, with a mean of 0.69-log units for PAHs, and 0.07- to 1.74-log units, with a mean of 0.41-log units for PCBs.

Predicted phase coefficients were compared to values reported in the literature. Most reference values for soot appear to have been obtained either by sorption studies on standardized reference materials, or on sediments from which natural organic carbon (and competition) have been eliminated, or they were developed from thermodynamic properties of the contaminants and the assumed sorptive phases. In most cases, these values appear to constitute an upper bound for sorption, or "intrinsic" sorption capacity, and have been observed by other researchers to be as much as an order of magnitude higher than observed coefficients in environmental samples. There are relatively few values reported for environmental samples in the literature. Such values are considered to be most comparable to those produced in this study, and those available generally support the predicted values based on uniform pore water concentration. Intrinsic values reported in the literature were generally within an order of magnitude of the predicted values for forms of black carbon thought to correspond to those in the study sediments.

Predicted coefficients obtained using a nonuniform pore water concentration corresponded more closely to intrinsic values than did coefficients obtained using a uniform pore water concentration. Literature values for black carbon-free OC coefficients, considered comparable to the OC and OG phases of the present study, corresponded within 0.06- to 0.28-log units, for combined OC/OG coefficients obtained using a uniform pore water concentration.

Predicted soot distribution coefficients and available reference values were plotted against log K_{ow} values for the compounds of interest. Reference values consistently increased with increasing log K_{ow}, with the exception of the few environmental values reported for natural sediments. These values decreased with increasing log K_{ow}. For the study sediments, either the distribution coefficients evidenced no dependence on log K_{ow} values, or the relationship was an inverse one, the coefficients decreasing with increasing log K_{ow}. The single exception to this were the PAH distribution coefficients obtained for the New York sediment, which were positively correlated to log K_{ow}. These results suggest that sorption of hydrophobic compounds, particularly PCBs, may be less dependent upon sorbate properties than indicated by studies on single sorptive phases where the effects of competitive sorption are not reflected. Flattening of values for the more highly chlorinated PCBs may also be explained by steric effects, retarding sorption of larger molecules and resulting in distribution coefficients comparable to smaller compounds of lower hydrophobicity.

In the density separations, some black carbon materials in the study sediments reported with the mineral fraction, implying a specific gravity greater than 2. This could suggest a relatively impure carbon phase, possibly less aromatic and with lower affinity for hydrophobic organic contaminants. For such materials, lower distribution coefficients would be expected. Alternatively, black carbon materials with specific gravity greater than 2 may simply be structurally similar to graphite, which has a specific gravity of 2.1. Mineral/carbon separation may be improved in density separations by the use of heavy media at a specific gravity of 2.1 or 2.2, but likely some overlap is unavoidable.

Desorption Resistant Fractions. The desorption resistant fraction of PAHs and PCBs was determined by mixing a sorbent (Amberlite XAD) with the bulk sediment to extract the readily desorbable contaminant fraction. The desorption resistant fraction of PAHs for the study sediments ranged from : Calumet, 0.34 (Anthracene) to 0.98 (Benzo[k]fluoranthene); New Bedford, 0.51 (Pyrene) to 0.88 (Benzo[b]fluoranthene); New York, 0.43 (Anthracene) to 0.85 (Benzo[b]fluoranthene). The desorption resistant fraction for PCBs ranged from: Calumet, 0.91 (PCBs 101 and 118) to 0.95 (PCBs 44 and 52); New Bedford, 0.75 (PCB 185) to 1.0 (22 PCB congeners); New York, 0.77 (PC 18) to 1.0 (PCBs 101 and 208). A distribution coefficient was calculated for the available and desorption resistant fractions, assuming the measured pore water concentration was attributable to the labile fraction. These were compared to predicted distribution coefficients for organic carbon, oil and grease and soot.

The ratio of the available fraction (PAH) distribution coefficient to the observed organic carbon normalized coefficient ($K_{OC, Avail}$ / $K_{OC, Obs}$) ranged from 0.66 to 0.96, with a mean of 0.87. If the assumption that the OC and OG are labile phases is correct, the ratio of the distribution coefficients for these phases should correspond to $K_{OC,Avail}$. Coefficient ratios less than one suggest that another phase may also contribute to the labile fraction. Results obtained suggest that the OC phase alone does not necessarily contain all of the labile contaminant fraction. For the both pore water assumptions, the mean ratio of predicted OC coefficient to labile coefficient was 1.07. The mean ratio for OC and OG coefficients combined to labile was

1.15 however, ranging from 1.02 to 1.60, for nonuniform pore water. These values suggest the presence of a non-labile component for one or both of these phases.

The ratio of the predicted soot coefficient to the resistant phase coefficient had a mean value of 1.03, with a maximum of 0.95, and minimum of 1.10 for the uniform pore concentration. The ratio was less than one for only 3 of 15 values, however. Ratio of soot coefficients based on nonuniform pore water to desorption resistant coefficient ranged from 1.19 to 1.41, with a mean of 1.30. On this basis soot could account for all of the desorption resistant fraction. Regression of desorption resistant PAH mass versus predicted PAH mass for soot, however, shows that the contaminant mass predicted for soot is insufficient to account for the entire desorption resistant mass in these sediments, supporting the concept of a distribution over multiple phases. Although these would appear to be somewhat contradictory results, the coefficient ratios were calculated for only a subset of the data, while the regression was conducted using the entire data set. The outcome of the regression analysis is therefore given slightly more weight with respect to this issue.

CONCLUSIONS

The value of fractionation studies in apriori estimation of contaminant reduction by separation of operationally defined fractions was demonstrated. The requirement of a favorable contaminant to sediment mass ratio in the fraction removed was established based on fractionation data from the study sediments.

Estimation of phase specific contaminant concentrations by regression of fractionation data appears to be feasible using a regression procedure robust to ill-conditioned data. The predictive value of contaminant concentrations associated with sorptive phases obtained by regression appears to be good for bulk sediment, but is less well demonstrated for individual size and density fractions. Regression on segmented data, divided by contaminant concentration range, might improve estimates in this regard. The estimates should still provide a reasonable basis upon which to tailor separation for removal of a specific sorptive phase, however, and extrapolation of expected contaminant reduction. This has the potential to improve process effectiveness and reduce the volume of residual contaminated sediments.

Distribution coefficients derived from the phase specific contaminant concentrations appear to be generally well supported, based on values reported for similar environmental samples and consistency with observed coefficients. Some improvement of the predicted values may be realized, however, with better understanding of the location of desorption resistant fractions and the relative contribution of each phase to the measured pore water concentrations. A six compartment model, representing available and desorption resistant fractions in oil and grease, soot and (non-black carbon) organic carbon, may be achievable. More accurate analytical definition of the sorptive phases may improve data quality and amenability to statistical analysis. These are areas that may prove fruitful in future efforts. Phase specific distribution coefficients are expected to be useful in assessing the potential mobility of contaminants in processed materials based not only on re-distribution of the contaminants, but on re-distribution of the sorptive phases. This should substantially strengthen the basis of partitioning analysis and associated environmental assessments.

APPENDIX

PERMISSION TO PUBLISH LETTER

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November 22, 2004

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Trudy,

You have my permission to use, include, or reprint as part of your dissertation the previously published Tech Notes we co-authored. These include:

> Olin-Estes, T.J. and Palermo, M.R. (1999). "Determining Recovery Potential of Dredged Material for Beneficial Use - Soil Separation Concepts," *DOER Technical Notes Collection* (TN DOER-C13), U.S. Army Engineer Research and Development Center, Vicksburg, MS. *www.wes.army.mil/el/dots/doer*
>
> Olin-Estes, T.J. and Palermo, M.R. (1999). "Determining Dredged Material Recovery Potential for Beneficial Use - Site Characterization: Prescriptive Approach," *DOER Technical Notes Collection* (TN DOER-C14), U.S. Army Engineer Research and Development Center, Vicksburg, MS.

Sincerely,

Michael R. Palermo, PhD, PE
Consulting Engineer

VITA

Trudy J. Estes was born October 22, 1953, in Kansas City, Missouri, moving with her family in 1959 to southwest Colorado, where she grew up and graduated from high school. She became interested in engineering and process design after working as a piping designer, drawing as-builts of oil production facilities in Aneth Field, Utah. She interned with Mobil Oil Corporation while pursuing a bachelor's degree in civil engineering from Colorado State University, graduating from there in 1992 with a growing interest in environmental engineering. She accepted a position as a research engineer at Waterways Experiment Station in Vicksburg, Mississippi, where she has since been involved with a variety of environmental engineering issues and projects. While working at Waterways she also completed her master's degree in chemical engineering (hazardous waste management focus) from Mississippi State University, graduating in 1996. She entered Louisiana State University in the fall of 1998 to pursue a Doctor of Philosophy Degree in the Department of Civil and Environmental Engineering. Having completed her research on contaminant distribution in sediments, she is now a candidate for that degree.